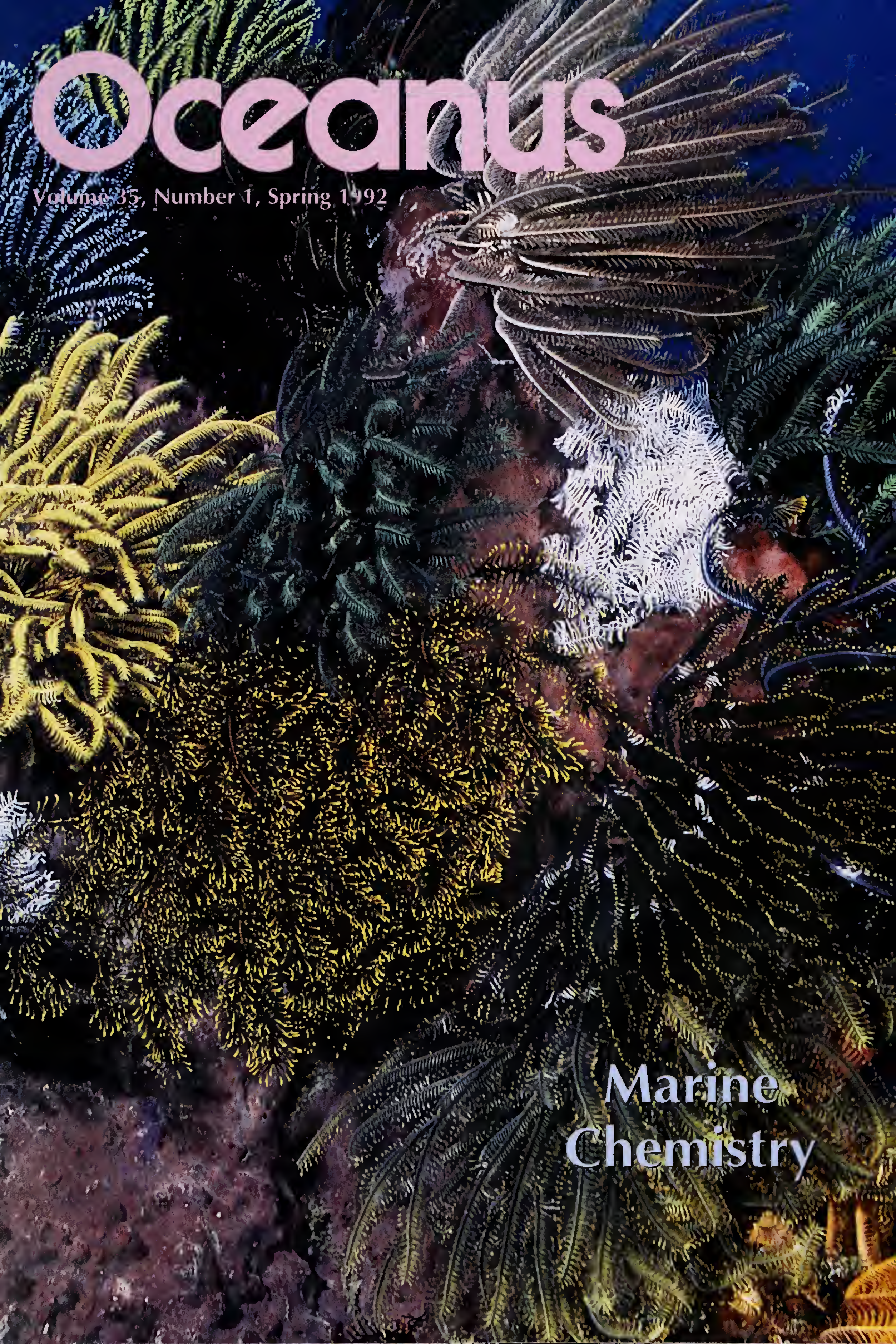
Oceanus

Volume 35, Number 1, Spring 1992



Marine Chemistry

R/V *Knorr* Returns to Sea

Tom Kleindinst

Following a three-year, mid-life refit, R/V *Knorr* is back at sea. *Knorr,* the largest Woods Hole Oceanographic Institution vessel, and sister ship R/V *Melville,* operated by Scripps Institution of Oceanography (University of California, San Diego), were both lengthened from 74 to 85 meters (245 to 279 feet). In addition, facilities were refurbished or upgraded, scientific laboratory and staging space was added, and berthing for scientists was increased. The refits were funded by the US Navy. *Knorr* was first out of the shipyard, arriving in Woods Hole in mid-October 1991 for final outfitting. The ship completed one cruise in the Atlantic for a RIDGE (Ridge Inter-Disciplinary Global Experiments) project, and then departed Woods Hole at dusk March 21 headed for an extended series of World Ocean Circulation Experiment cruises in the South Pacific. *Melville* left the refit yard March 14 for San Diego and final outfitting there. The ship returns to sea in mid-summer.

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MARINE CHEMISTRY

E. Paul Oberlander

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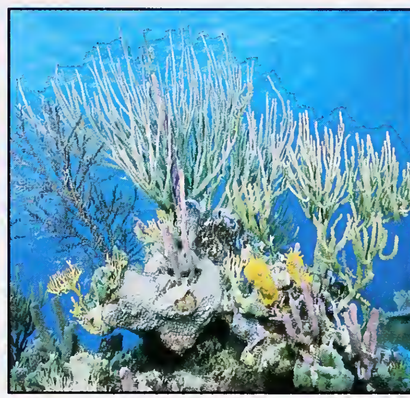
Jeremy Stafford-Deitsch



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James E. Broda

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DEPARTMENTS

ON THE COVER: Jeremy Stafford-Deitsch photographed these relatively common sea lillies (or crinoids) in unusual splendor off Papua, New Guinea. To catch a glimpse of what these may look like hundreds of millions of years from now, see page 38. Stafford-Deitsch's latest publication is *Reef, A Safari Through the Coral World* (Sierra Club Books, San Francisco, CA © 1991).

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From the Editor

1992–An Ocean Science Voyage

Oceanography encompasses all the basic sciences as they apply to the marine world. The formal organization of oceanographic institutions and funding agencies tends to reflect this: the departmental structure of the Woods Hole Oceanographic Institution, for example, includes departments of biology, marine chemistry and geochemistry, physics, and geology and geophysics, as well as applied ocean physics and engineering.

There's a lot of interdepartmental interaction, of course. Marine chemists need to know about the animals that live in the sea in order to understand the chemical composition of the water and the sediments below it. The animals living in the water are affected by its chemistry and its motion or physics. Animal remains and products affect the sediments, and so does seawater chemistry. Elements extracted from rock through hydrothermal circulation alter seawater chemistry. Currents move chemicals around the ocean basins. It's a circular business.

But, still, the basic discipline is the parent of the marine discipline, and oceanographers tend to think of themselves as both oceanographers and chemists, biologists, geologists, physicists—and sometimes as such hybrids as geochemists.

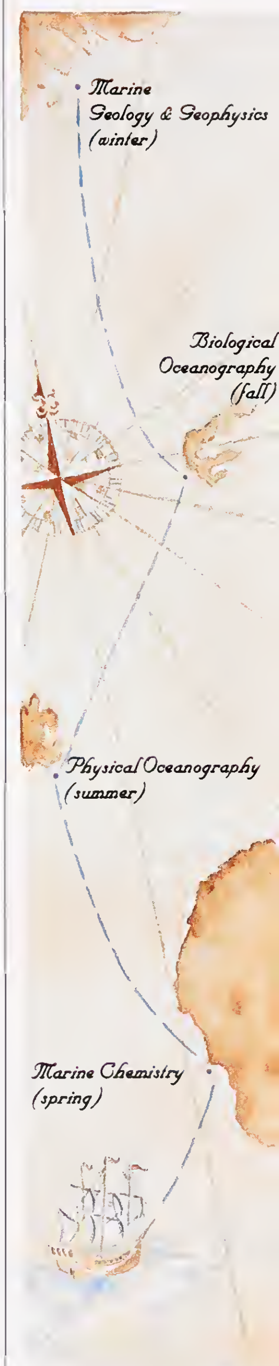
The 1992 volume of *Oceanus* is also organized along these disciplinary lines. In this, the first issue of 1992, we offer an overview of marine chemistry followed by nine articles on topics that fall generally into this discipline. This is not a comprehensive treatment of marine chemistry; rather, it is a look at some underlying principles of the field and a few interesting topics within it.

All four issues this year will follow this approach. Physical Oceanography is next in the Summer issue, then Biological Oceanography in the Fall, and Marine Geology & Geophysics for Winter 1992/93. Together they will constitute something of a primer in the ocean sciences.

Beginning with this issue, we will also bring you a regular set of departments. Ocean Law & Policy offers views on marine issues such as the "precautionary principle" that author Jim Broadus classifies as the unique modern creature, *Principium precautionarium*. It is patterned, of course, on another department, Creature Feature, that introduces one of the sea's interesting inhabitants. This issue's featured creature is the Spanish dancer nudibranch, a beautiful (but bad-tasting) denizen of the deep. Oceanographer's Toolbox reveals some secrets (and headaches) of instrument design for a wet, salty environment, and Focus on the Coast zeroes in on the waters best known to the human creature.

This is a special year for *Oceanus*—it's our 40th year. The first issue appeared in Winter 1952. (You may notice that this is Volume 35. That's because our earliest volumes encompassed more than one year.) Welcome to our year-long, 40th-anniversary tour of oceanography. Send us a postcard and let us know how you enjoy the trip!

Vicky Cullen



E. Paul Ober

Ocean Law & Policy

Creature Feature Too: *Principium precautionarium*

James M. Broadus

No way can a column on law and policy hope to grab "normal" readers the way a colorful and exotic Creature Feature can. So think of this department as a Creature Feature too, sort of. Prepare to meet a recently discovered (in fact, newly evolved) marine creature that has never been photographed. Like Nessie of Loch Ness, who *may* have been photographed, there is also some doubt about this creature's existence. Descriptions vary widely and sometimes conflict; it seems to take many forms. This is a creature of international law and environmental regulation. It is called the "precautionary principle."

The precautionary principle is intended to answer the question, "What rule should we follow to make prudent choices in the face of scientific uncertainty?" The context is usually environmental regulation, especially choices about permissible levels of economic activity or associated chemical emissions. Different types and levels of emissions obviously can cause different types and levels of environmental harm, but reducing or prohibiting the emissions costs something too, at least in terms of foregone benefits from the emissions-producing activity. If regulators knew what losses would result from given levels of emissions, they could balance them against the offsetting losses from reducing or prohibiting the emissions and thus calibrate an appropriate, permissible level. In some cases this level may be zero, but in others, absorbing *some* environmental impact may be worthwhile. Because of the complexity of most biochemical interactions and the long-term nature of many biogeochemical effects, however, scientific uncertainty is the norm. Rather than reckoning with known environmental damages, the regulators are working against the risk of damages.

The precautionary principle directs regulators to preempt or eliminate this risk. A typical formulation was issued by the Nordic Council's 1989 Conference on Pollution of the Seas, calling for "an effective precautionary approach, with that important principle intended to safeguard the marine ecosystem by, among other things, eliminating and preventing pollution emissions where there is reason to believe that damage or harmful effects are likely to be caused, even where there is inadequate or inconclusive scientific evidence to prove a causal link between emissions and effects." On the face of it, this merely states the perfectly reasonable guideline that proof of harm is not required to control or prohibit the release of possibly harmful substances into the environment.

Originating in German water-quality policy in the 1980s, this approach has been incorporated mainly into international arrangements for protection of the marine environment. Versions are found, for example, in intergovernmental regional agreements to control marine pollution in the North Sea and the Baltic, as well as in the Mediterranean and other Regional Seas programs organized by the United Nations Environment Programme (UNEP). A definition is currently being negotiated for application to the London Dumping Convention, which governs ocean dumping practices worldwide.

The precautionary principle now shows signs of spreading rapidly beyond the marine environment. Draft language contained in the Working Document for a

Framework Convention on Climate Change, under negotiation for adoption at the June United Nations Conference on Environment and Development (the "Earth Summit"), states "...precautionary measures to meet the climate challenge must anticipate, prevent, attack or minimize the causes of, and mitigate the adverse consequences of, environmental degradation that might result from climate change....lack of full scientific certainty should not be used as a reason for postponing measures...."

Interpretation, of course, makes a difference. For example, the statement of the 1991 International Conference on an Agenda of Science for Environment and Development into the 21st Century (ASCEND 21) speaks of "the central importance of the precautionary principle, according to which any disturbance of an inadequately understood system as complex as the Earth system should be avoided." *Any* disturbance? At *all* costs?

The problem with the precautionary principle is that it is not a principle at all, but a range of more-or-less rhetorical prescriptions for choice in the face of uncertainty. At its best—in permitting controls even where scientific proof of harm is lacking—the precautionary principle tells us nothing new about how to make prudent decisions. Rational decisions have always involved making judgments about the probability and magnitude of adverse consequences and weighing these against the probability and magnitude of beneficial outcomes. Such calculations can and usually do include recognition and accommodation of people's aversion to risk by factoring in a "risk premium" or some margin of safety. The real difficulty is in estimating the probabilities, benefits, and costs, and in gauging the risk premium or safety margin. The precautionary principle offers us no guidelines, unless it tells us to set the risk premium or safety margin at infinity, thereby prohibiting everything with any environmental risk, however small.

Thus, at its worst—in effect requiring proof of no harm before permitting any activity—the precautionary principle is a prescription for absurd and self-defeating choices that completely ignore any reasonable balancing of benefits and costs. Adoption of this extreme form risks squandering limited resources and losing real potential benefits. As alternatives are employed, it may also shift environmental risks to other media (for example, from ocean ecosystems to groundwater supplies in the case of outlawed ocean waste disposal). University of Washington legal scholar Daniel Bodansky has made the point succinctly: "The precautionary principle seems to suggest that the choice is between risk and caution, but often the choice is between one risk and another." Almost always, in fact.

If the precautionary principle is to become an integral part of our environmental policies, as now seems probable, a "rule-of-reason" version is needed. Until that is available, this peculiar creature should be approached only with great caution.

James M. Broadus, an economist, is director of the Marine Policy Center at Woods Hole Oceanographic Institution.

Heiser Zedonek

Oceanographer's Toolbox

Benthic Landers: Taking the Laboratory to the Seafloor

Fred L. Sayles

Though extremely remote and inaccessible, the vast expanse of seafloor that averages 4.8 kilometers depth below the ocean surface is nevertheless of great importance. It is, despite its remoteness, an integral part of the ocean-atmosphere system. Processes occurring there influence the removal of material from the ocean-atmosphere system, the productivity of the surface ocean, and the historical record of Earth's surface conditions that lie buried in the sediment.

The importance of ocean-floor sediments to understanding ocean chemistry, the fate of materials in the ocean, and past and future climate changes long ago led oceanographers to develop methods of sampling and studying them. Systematic sampling dates at least to the *Challenger* Expedition (1872 to 1876), and extensive sediment coring has been done for decades. Only recently, however, has it been possible to make on-site measurements and carry out experiments on the seafloor that greatly enhance our understanding of the chemical and biochemical processes occurring at and just below the water-sediment interface. Key among equipment that has brought experimental accessibility to the seafloor is a class of instruments called benthic landers, pioneered in large part by Ken Smith of the Scripps Institution of Oceanography (University of California, San Diego). These landers are really a variety of instrument systems packaged into a single "vehicle" that carry out sampling, experiments, and analyses while resting unattended on the seafloor for weeks to months at a time.

Bringing the laboratory to the seafloor has not been easy, or without its costs in time, energy, anxiety, and money for those pursuing this line of research. These computer-controlled instrument systems are complex, and their modes of failure are correspondingly varied and mysterious. Achieving operational status requires a high level of technical expertise, commitment, determination, stubbornness, and, on occasion, luck.

Over the past six years we have been developing and, more recently, using one of the more complex benthic landers. While only in use for a few years, it has already begun to provide new insight into the link between events occurring at the surface of the ocean and processes on the seafloor. Our measurements of reactions on the seafloor clearly show that benthic processes respond rapidly to changing conditions at the surface. This lander's capabilities are indicative of what can be done on the seafloor with the present generation of instruments. The near future promises still greater capability—but the requirements for success, noted above, as well as the trials and tribulations, will no doubt remain much the same. What follows briefly summarizes the the lander's capabilities and some of our experiences during the development process. Conversations with colleagues indicate the story is not atypical.

The ROLAI^{2}D Lander

All self-respecting, relatively unique instruments must have an acronym or face eternal anonymity. Our lander was, after several years of development, dubbed ROLAI^{2}D. The similarity to a well-known antacid used to quell the consequences of prolonged stress and anxiety is not in the least coincidental. Those first years contained more cases of "unlikely" or "impossible" sequences of events (all negative) than I care to

remember. The use of various stomach remedies became an integral part of our routine. This determined the character of the name, leaving only the choice of a list of compatible words to match the acronym. The lander was duly christened with champagne (prior to the advent of dry ships) as ROLAI^{2}D: Robotically Operated Lander for the Analysis of Interstitial and Interface Diagenesis. In English, this simply means a lander for the study of biogeochemical reactions at and near the interface between the sediments and the oceans.

ROLAI^{2}D was designed with three goals in mind:
1) to directly measure the reactions occurring on the seafloor (this is the most basic information needed to understand the transformations that settling materials undergo as they become part of the sedimentary record);
2) to determine where reactions occur—specifically, whether material reacts as it lies on the surface of the sediment or after it is buried; and
3) to estimate how much of the material arriving at the seafloor is returned to the oceans as a result of reaction, and what controls the proportions that are recycled versus buried (this provides the key to reading the record of past oceans that is preserved in the sediments).

It is in meeting these objectives that the analogy to a seafloor laboratory becomes apparent. To acquire the data we need, the instrument package manipulates samples, adds chemical tracers, carries out chemical analyses, tests the condition of equipment on the platform, makes decisions based upon the test results, and sends information to a surface ship. As in any modern laboratory, much of the work is computer controlled.

While ROLAI^{2}D is loaded with microelectronics, the equipment needed to complete its program makes the lander itself anything but micro. With its various flags for visibility and antennae for communication with ships and satellites, ROLAI^{2}D stands over five meters tall and weighs more than 2,000 kilograms in air. However, it is neutrally buoyant, that is, it weighs essentially nothing, as it approaches the ocean bottom. The photo below shows the lander being launched from the fantail of the Bermuda Biological Station's R/V *Weatherbird*. The round, tan, syntactic-foam structure atop ROLAI^{2}D provides buoyancy to bring the lander to the surface at the end of a deployment. The pads upon which it stands are the ballast released to initiate ascent to the surface. They double as foot pads while ROLAI^{2}D is sitting on the sediment surface. The orange case at lower left is one of three batteries that provide power for operations on the seafloor. In the photo (overleaf), the lander settles to the bottom under the watchful eyes of divers in shallow-water tests.

Matt Doty

Researchers aboard R/V Weatherbird *prepare ROLAI^{2}D for a sojourn on the seafloor.*

ROLAI^{2}D is a free vehicle, as it is not tethered to the ship. For deployment, ROLAI^{2}D is picked up from the deck and lowered into the water (via the ship's winch), the handling cable is then released, and the lander descends to the seafloor completely disconnected from the ship. ROLAI^{2}D's computer checks the landing sensors during descent and reports their status to the ship's laboratory as a set of pings that is monitored by the ship's depth recorder. On approach to the bottom, buoyancy is adjusted to insure a very slow and controlled landing, which is essential to avoid disturbing the easily suspended material lying on the sediment surface. Sensors tell the computer when ROLAI^{2}D has landed, and a second buoyancy adjustment increases the "weight" of the lander by 113 kilograms to provide stability during the experiments. Then ROLAI^{2}D initiates its preset sequence of experiments. As chambers descend into the sediment to isolate portions of the bottom for the experiments, ROLAI^{2}D's computer confirms a successful initiation sequence, and the ship leaves the site.

ROLAI^{2}D continues its experiments, analyses, and sampling for several weeks. At the end of the programmed experiment, we return to the site and send a "continue" command that initiates final experiments as well as a "close-down" sequence to retract ROLAI^{2}D's sensors and equipment for protection during recovery. The last bottom event is the release of 275 kilograms of ballast, permitting the instrument to lift from the seafloor and start its 4.5-kilometer ascent to the surface.

The above is the planned sequence and one hopes never to experience deviations from it. Such is rarely the case. Failures and the unforeseen always plague the developmental stages of devices such as ROLAI^{2}D, and remain a constant threat during use. To be successful, dozens of components must work in tandem. One fear, however, overshadows all others in the use of free vehicles: failure to release from the bottom. At depths of 4 to 6 kilometers, these vehicles are beyond the reach of all but the deepest-diving submersibles; even if ROLAI^{2}D could be found by submersible, little could be done beyond nudging the instrument in the hope of freeing it. Grappling for it is analogous to using a fishing line from the top of the Empire State Building to hook the handle of a bucket on the ground below—at night!

This fear became reality on ROLAI^{2}D's very first deep-ocean deployment. The launch was completely successful, and on return for recovery a month later we established command contact, initiated the completion sequence, and received acknowledgement on the first try, to our tremendous relief. However, that was to be the last we heard from the onboard computer.

Matt Doty

Watchful divers hover near ROLAI^{2}D as it settles to the seafloor in shallow-water tests.

The times scheduled for data reports came and went in dead silence, interrupted only by bubbling noise from wash on the ship's hull. We had prepared for the loss of the computer with two emergency release systems. After two of the longest hours of my career, we activated one of these backup systems and monitored the lander's position relative to the seafloor. Nothing. ROLAI^{2}D remained fast on the bottom, miles below the ship. After an agonizing hour of waiting and listening in vain for signs of release, and after having been awake for nearly 24 hours, we agreed to try to get a few hours of sleep before making any further decisions. I spent the two hours wondering what to say to our sponsors and how to convince them that the lander was still an important concept worth pursuing; sleep was not in the cards. At 3 AM, I went to signal the lander once more.

Wayne Dickinson, the architect of much of the lander, had a better idea at about the same time. While I was greeted with continuing silence, he was donning earphones to listen for the radio signal ROLAI^{2}D emits on the surface. Rather than silence, he was greeted with the warble we have come to love and await with considerable anxiety: the "I'm on the surface, come and get me" signal.

ROLAI^{2}D had broken free as we tossed and turned in our bunks and was some five miles downwind, flashing its light and sending a strong radio signal to direct recovery. It has been four years and over a dozen deployments since the black of that night. ROLAI^{2}D has behaved admirably in that time, performing at the level we had hoped for, and returning faithfully on command.

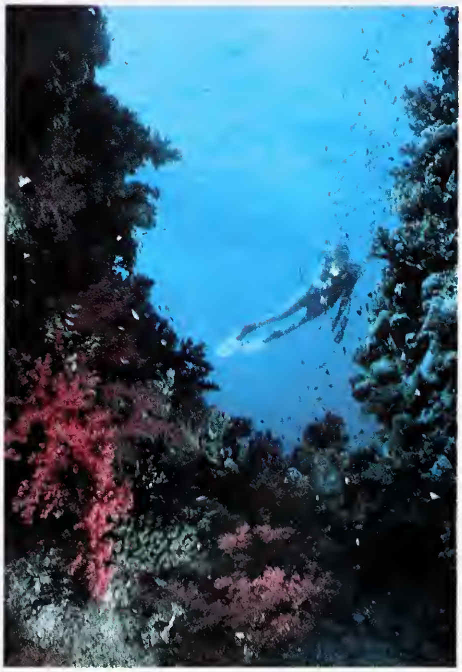
Fred Sayles is a Senior Scientist in the Department of Marine Chemistry and Geochemistry at Woods Hole Oceanographic Institution.

Marine Chemistry

John W. Farrington

The oceans are a complex chemical soup. Marine chemists apply a variety of sophisticated instruments to defining the soup's chemical composition and the processes that control it, and to unravelling the biochemistry of the organisms that live in it. Their research advances general knowledge of the oceans and of chemistry, and frequently has immediate, profound implications for wise stewardship of local, regional, and global habitats.

Seawater's saltiness has fascinated scholars and philosophers since antiquity. Several renowned 17th and 18th century chemists, for example Robert Boyle and Antoine-Laurent Lavoisier, analyzed seawater for salts. Systematic chemical exploration of the sea probably began with Alexander Marcet's analysis of seawater in the early 1800s: He found that the major salts he could detect seemed to be in constant proportion to one another, even though the total amount of salt varied from sample to sample. Later Georg Forchhammer expanded significantly on Marcet's work, and a major step forward followed shortly with analysis of seawater collected during the *Challenger* Expedition (1872 to 1876). Studying these samples from all over the world, William Ditmarr elaborated on Marcet's principle to arrive at what we now call Dittmar's Law: the proportions of seawater's major chemical constituents are constant within a very small range.



© Rick Sammon

Coral reefs hold potential for natural marine chemicals, as D. John Faulkner discusses beginning on page 29. (Photo from Seven Underwater Wonders of the World, *to be published in October 1992.)*

Since then, many studies have confirmed and expanded upon Dittmar's Law. We know the relative proportions of several major chemicals in seawater do not change markedly from one place to another in the oceans, and they have remained essentially the same for at least thousands to millions of years. Some other chemicals vary in time and space according to the influence of input and removal processes. These chemicals become useful tracers of oceanic processes, as explained inMarine Organic Geochemistry on page 38 and Tracers in Oceanography on page 47.

The major chemicals dissolved in seawater exist in the ionic form, and contribute to seawater's ionic strength. (Ions are atoms or groups of atoms that have positive or negative charges as a result of having lost or gained one or more electrons.) As anyone who tries to maintain an automobile in a coastal area knows, seawater is a very corrosive medium. Marine chemists work in concert with materials chemists and engineers to understand and prevent or reduce corrosive processes. This is but one example of the challenges that modern marine chemistry addresses.

Edward T. Peltzer III

Towers like this one, constructed in American Samoa for the Sea-Air Exchange Program, are used both ashore and on ships for studies of marine atmospheric chemistry.

In this issue of *Oceanus*, we explore some aspects of modern marine chemistry. We have made no attempt to be comprehensive in our coverage; instead, we focus on a few important issues that currently engage marine chemists, as examples of the richness and challenge of this science.

Marine Chemistry Today

Marine chemists are sometimes called chemical oceanographers or marine geochemists, depending on their particular research focus, but designations are not important. The common factor is the study of the chemistry of something related to the oceans: seawater, air over the oceans, sediments, land margins and rivers, or biota. Marine chemists cannot productively pursue their work in isolation. Advances in fundamental chemistry underpin those in marine chemistry, and marine chemists collaborate with physical oceanographers, biological oceanographers, marine geologists and geophysicists, oceanographic engineers, and atmospheric scientists.

The fascinating questions marine chemists address include:

- How much of the fossil-fuel carbon dioxide released to the atmosphere by our civilization's energy sources is taken up by the oceans, thus moderating the greenhouse effect (the retention of heat within Earth's atmosphere, instead of the release of heat into space)?
- To what extent are the oceans sources or sinks for other greenhouse gases such as methane?
- How were the oceans formed, and how have they changed over geological time?
- How do chemicals of environmental concern such as pesticides, petrochemicals, petroleum compounds, metals, and radioactive chemicals from nuclear wastes or weapons testing enter and move through the oceans?
- Where and for how long will marine organisms be exposed to detrimental concentrations of these chemicals?
- Are consumers exposed to unacceptable risk if they consume seafood?
- Are there natural chemicals produced by marine organisms that can benefit modern civilization?
- What processes control the natural biological productivity of the oceans?

The challenges I have broadly outlined are not new: They have been at the heart of marine chemistry for decades or longer. Coverage of global climate change in the popular press might lead one to think that concerns within the scientific community about the carbon dioxide "greenhouse problem" is a phenomenon of the past five years. Not so! For example, in June 1964 the American Chemical Society's weekly

Chemical and Engineering News ran an article titled "Chemistry and the Oceans" that included several paragraphs under the heading "Greenhouse effect may be causing an over-all warming of the earth." Thus 28 years ago marine chemists were discussing efforts to understand the increasing carbon-dioxide concentrations in the atmosphere and how the oceans might be involved in the global carbon cycle.

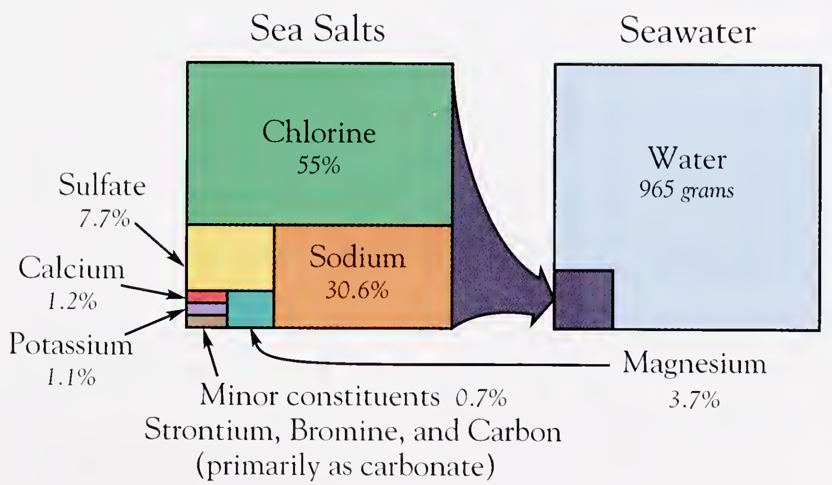
Marine chemists, physical oceanographers, atmospheric chemists, and climate modelers have made progress in understanding the biogeochemical carbon cycle in the contemporary and ancient world, and the cycle's relationship to climate. (See Balancing the Budget, page 18; Tracers in Oceanography, page 47; Particles in the Oceans, page 60; JGOFS, page 57; and Marine Organic Geochemistry, page 38.)

The Origin and Composition of Seawater

The chemical constituents of seawater originate mainly from three sources:

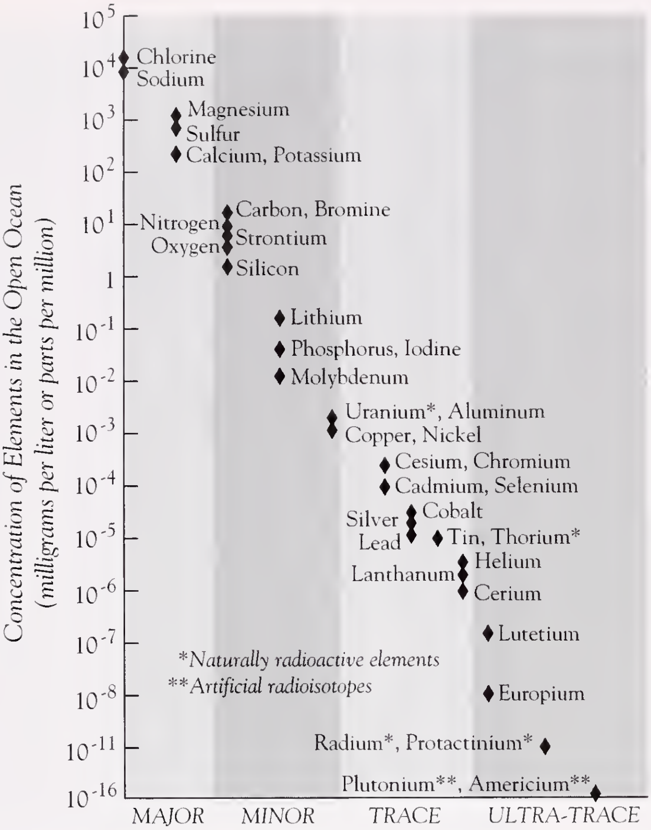
- Degassing (releasing volatile chemicals) of Earth's mass that began after the planet's formation and continues today in certain types of volcanic activity that produces water, some carbon, chlorine, nitrogen, and sulfur;
- Erosion of sediments and basalts (rocks of volcanic origin) on land by the weathering activities of rain, wind, sunlight, and atmospheric gases (mainly oxygen) that contributes chemicals to the oceans via rivers or the atmosphere; and
- Seawater reactions with basalt extruded under the sea that release chemicals to seawater and also transfer others from seawater to basalt. (See Hydrothermal Activity in the Deep Sea on page 76).

Additional sources of seawater chemicals are biological processes that produce organic chemicals and cycle bioreactive elements through various chemical forms, photochemical reactions that occur in the ocean's upper reaches (see the Box on Photochemistry in the Oceans, on



Jack Cook/WHOI Graphics

As a group, salts are an important constituent of seawater. Relative proportions of predominant seawater salts are shown.



Jack Cook/WHOI Graphics

The primary chemical constituent of seawater is water, but numerous other chemicals are also present. Some seawater chemicals exist in such low concentrations that identifying their presence is a challenge in itself, and quantifying them yet another difficult matter.

page 36), and the radioactive decay of elements that yields other elements. Over millions of years these processes have culminated in the seawater of today's oceans.

The major chemical constituent of seawater is water. It is a very valuable chemical; in arid regions, desalination plants produce life-giving fresh water from the salt water of the sea. This fact gained new significance during the recent war in the Persian Gulf when oil spills threatened several desalination plants. Over geological time the balance of water between the ocean, the atmosphere, and the ice caps and glaciers has been a key facet of climate. Water, as a vapor, is a primary greenhouse gas, and water-vapor accumulations as clouds are another significant aspect of the energy balance between incoming radiation that heats Earth's surface and outgoing radiation that cools it.

Seawater's chemical constituents include many elements whose concentrations are exceedingly low—some so low that their analyses pose formidable challenges; periodically, in the past three decades, some "known" concentrations have been revised downward as it was discovered that their measurements were made in samples contaminated by the sampling container, the ship, or in the laboratory. A story that illustrates this point is told to most beginning chemical oceanographers. According to Karl Turekian (Yale University), the German chemist Fritz Harber explored the possibility of extracting gold from seawater in the 1920s. He reasoned that even though the gold concentration was about one part per billion, the vast ocean waters contained 10 million grams or 11 tons. (At today's prices, that would be worth about $118 million.) Harber's efforts to conduct a pilot project failed to recover large quantities of gold. Instead, he discovered the reported concentrations were in error; the gold concentration was about 1,000 times lower! This brought his project to an end because the cost of extraction would exceed the value of the gold recovered.

As Authors Edmond and Von Damm point out (Hydrothermal Activity in the Deep Sea, page 76), mineral deposits are forming on the seafloor near hot vents. These are not economically viable deposits at present, but their study tells us important things about where to look for certain kinds of ore deposits (see also *Oceanus*, Winter 1991/92).

A panoply of chemical and biological reactions in seawater and the underlying sediments influences seawater's composition. Readers who have had an introductory course in chemistry will recognize the processes that govern the composition of seawater: acid-base reactions,

oxidation-reduction, radioactive decay, precipitation and dissolution, and ionic strength and activity coefficients. On a very basic level, the differences between the laboratory of the oceans and the freshman chemistry laboratory (at least as I remember it) are the large number of chemicals involved in the experiments and the complexity and intricacy of the myriad chemical processes occurring simultaneously in the oceans.

Biogeochemical Cycles and the Oceans

We have already mentioned carbon dioxide and the ocean's role in the global carbon cycle. One thing to keep in mind about these biogeochemical cycles is that we are uncertain of the exact exchange rates between their various reservoirs, and, in a few cases, the reservoir sizes. For example, we don't know precisely how fast microscopic plants of the sea, the phytoplankton, convert carbon dioxide to organic matter by photosynthesis, or how quickly the organic matter is converted back to carbon dioxide by metabolism. Where this metabolism occurs is another factor in our uncertainty about the global biogeochemical carbon cycle, and therefore contributes to our significant uncertainty concerning climate models that depend on coupling the carbon cycle with the amount of carbon dioxide in the atmosphere. This in turn becomes material for political debates regarding recommended policies for energy utilization in developed and developing countries.

A variety of approaches address the intricacies of the global carbon cycle. An improved understanding is critical to wise stewardship of the planet, and we cannot afford to rely on only one research approach. We need, indeed require, independent checks of the workings of the biogeochemical cycles. A recent finding illustrates this point. Japanese marine chemists Yoshimi Susuki and Yukio Sugimura (Meteorological Research Institute, Tokyo, Japan) reported three years ago that measurements of dissolved organic carbon (all forms of organic chemicals dissolved in seawater expressed in concentration units of carbon) by a modified method of high-temperature catalytic oxidation were two- to three-times higher in some areas of the ocean than previously reported. Should their measurements prove correct, then the dissolved organic carbon in the oceans is significantly higher than we thought, and one part of the biogeochemical carbon cycle must be revised vastly upwards (by much more than the amount of carbon released to the atmosphere each year from fossil-fuel combustion). As we go to press, marine chemists on a JGOFS expedition (see page 57) are double-checking Susuki and Sugimura's findings. This is an example of a fundamental tenet of science in action: independent replication of results.

What is a Biogeochemical Cycle?

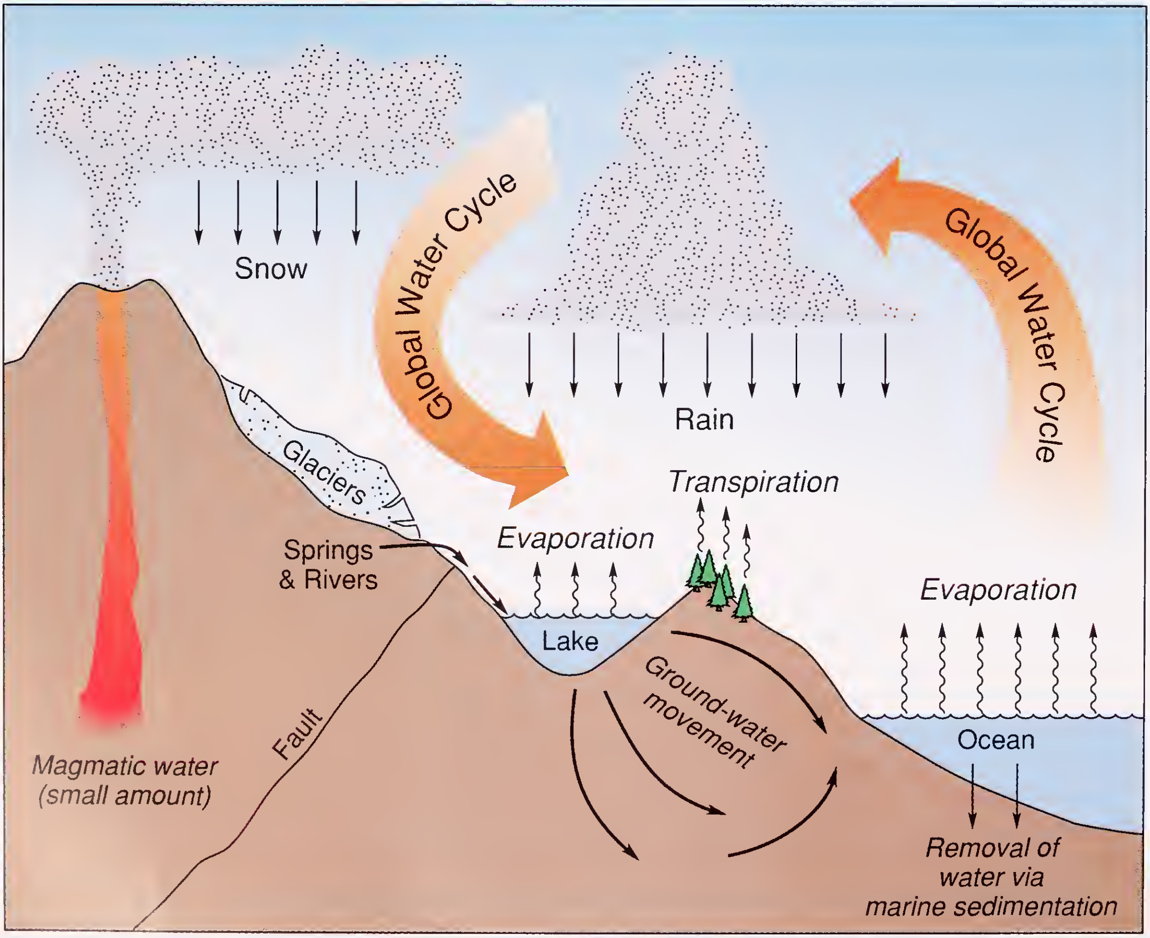
Biogeochemical cycle is a term that describes the pathways and movement rates of chemicals in land, the atmosphere, ocean systems, and, in many cases, Earth's crust. The exact form of a chemical and its physical state (such as dissolved, particulate, gaseous, or nongaseous) can be controlled by *bio*logical, *geo*logical, and *chemical* processes—thus "biogeochemical." The "cycle" part comes from the fact that over varying periods of time, chemicals travel once or many times around the same or similar pathways, completing cycles. Actually, we find there are many biogeochemical cycles within larger and larger biogeochemical cycles when we investigate time scales ranging from minutes to millions of years, and space scales from individual marsh creeks to entire oceans.

The global water cycle, and the many cycles that operate within it, are subjects of study for marine chemists. Over geological time, the distribution of water among the oceans, atmosphere, and glaciers varies and is a key facet of climate. Particles that move with water (as ice, liquid, and gas) give yet another set of clues to be investigated.

Chemicals as Tracers of Oceanic Processes

One of seawater's naturally occurring trace elements is uranium. It is present as three main isotopes or related forms, distinguished from one another by the number of neutrons in the nuclei. These forms are also radioactive, and decay via a chain of nuclear reactions to yield various other elements. From a marine-chemistry perspective, there are two important features about these decay series: the half-lives and the chemical properties of the elements in the series. By measuring the various isotopes in dissolved, colloidal (ultra-small particles), small-particle, and large-particle phases of seawater at many locations using trace analytical-chemistry methods, marine chemists can assess particle-settling velocities, sediment-accumulation rates, the rate at which bottom-dwelling animals pump water through surface muds, and gas exchange between the ocean and the atmosphere. Because the "clocks"—the radioactive decays—and the chemical properties of the elements are both well known from fundamental chemistry, naturally occurring trace chemicals can be used to study oceanic processes.

In his eloquent description of how marine chemists approach ocean processes using other chemicals as tracers, Bill Jenkins (Tracers in Oceanography, page 47) modestly leaves out the details of the care and precision such measurements require and the fact that in many cases



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marine chemists must design and build their own instruments (such was the case for Bill's measurements of helium isotopes), or extensively modify off-the-shelf instruments.

During the 1970s, as part of the International Decade of Ocean Exploration, the Geochemical Ocean Sections program (GEOSECS) conducted cruises throughout the world to collect a modern set of measurements on a wide array of chemicals including major forms of carbon (bicarbonate, carbonate, and carbon dioxide), oxygen, and trace radioactive elements such as the uranium decay-series elements previously discussed. In the early 1980s, the Transient Tracers in the Oceans program repeated some of these measurements.

A combination of small-scale oceanographic cruises that last several weeks, larger multiyear systematic cruises such as the GEOSECS efforts, and individual laboratory studies of chemical processes provide an overall picture of biogeochemical cycles in the oceans.

On Becoming a Marine Chemist

The principle investigators or leading scientists for marine chemistry projects come from varied educational backgrounds. Some were undergraduate chemistry, physics, biology, geology, or earth science majors who studied chemical oceanography or geochemistry in graduate school. Others studied chemistry or physics in graduate school and entered marine chemistry early in their post-doctoral careers. They are assisted in these projects by scientists with a range of undergraduate backgrounds including the fields mentioned as well as electrical engineering and computer sciences. The common factor for these scientists is a strong background in a major field of science, including several college-level math courses (through differential equations) and a few courses in other science disciplines.

Ocean Pollution

Marine chemists, in concert with their colleagues in the other ocean sciences, have made substantive contributions to understanding the inputs, fates, and effects of many chemicals that enter the oceans and are of environmental concern. The knowledge gained has had a major influence on policy with respect to environmental problems, ranging from the ban on indiscriminately using chlorinated pesticides such as DDT, limiting and stopping production of selected industrial chemicals such as polychlorinated biphenyls (PCBs), regulating oil inputs to the sea, and regulating disposal and discharge of wastes into the ocean.

The past 20 years have been exciting ones for marine chemists. We have progressed from mainly descriptive, qualitative, but tremendously important pioneering studies that detected the presence of marine chemical contaminants and pollutants to the quantitative understanding of their properties and the processes governing their movement through the marine environment. We are on the threshold, via sustained research efforts over the 1990s, of being able to predict biogeochemical cycles and the effects of environmentally significant chemicals.

John W. Farrington is Associate Director for Education and Dean of Graduate Studies, and a former Senior Scientist in the Chemistry Department at the Woods Hole Oceanographic Institution (WHOI). While doing research as a biochemistry graduate student in 1968 he visited the library at the Marine Biological Laboratory in Woods Hole. On a break from library reading he happened upon WHOI's Redfield Auditorium, where a noontime seminar introduced him to the challenges and fun of oceanography. John changed his career plans from biochemistry to oceanography and came to WHOI in 1971. His research interests are organic geochemistry, biogeochemistry of chemicals of environmental concern, education, and science-policy-management interfaces.

Balancing the Budget

Carbon Dioxide Sources and Sinks, and the Effects of Industry

Taro Takahashi, Pieter P. Tans, and Inez Fung

Many observations support the notion that greenhouse warming is already occurring.

Molecules of carbon dioxide (CO_2) and other trace gases absorb infrared radiation or heat. An atmospheric increase in these infrared-absorbing gases, which include water vapor, methane, and chlorofluorocarbon (the Freons or CFCs) would permit less heat to escape from Earth's surface into space. The atmosphere would retain more heat, in the way a greenhouse holds heat, and this "greenhouse effect" may be accompanied by some dire consequences: Regional desertification, dramatic sea-level rise, and an increase in both the frequency and intensity of hurricanes have been predicted.

Greenhouse gases are measured regularly (from hourly to monthly, depending upon the intended purpose) all over the world, and chemical analyses of air bubbles trapped in old glacial ice provide pre-industrial concentrations. These measurements show that the atmospheric carbon dioxide concentration has increased by 25 percent since the pre-industrial period (1750 to 1800), from about 280 parts per million then to 350 parts per million by volume today. The concentration of methane has nearly doubled, from about 800 to 1,700 parts per billion since the pre-industrial time. The CFCs have gone from zero, prior to 1950, to about 600 parts per trillion today.

Many observations support the notion that greenhouse warming is already occurring. For example, global sea level has been increasing at a rate of 15 to 25 centimeters per century during the past 100 years, perhaps due to glacial melting in polar regions and thermal expansion of seawater. Global mean air temperature (computed using select sets of meteorological observations) exhibits a warming trend of about 0.7°C since 1880. Variations in the oxygen isotope ratio found in deep ice cores from Greenland and Antarctica infer a temperature record for the past 160,000 years, which includes the last major Ice Age ending about 12,000 years ago. We find that the temperature record correlates very well with carbon dioxide concentration measured in air bubbles trapped within ice crystals: higher temperatures and higher carbon dioxide concentrations are coincident. The 0.7°C warming over the past 100 years is substantial,

Ian Worpole

even when compared with temperature excursions Earth has experienced over geological time.

We must be careful when interpreting these observations, however. On the one hand, it is not possible to tell from the data presented in the figure on the next page whether the increase in atmospheric carbon dioxide concentration in the past 160,000 years has caused the global warming or, vice versa, the warming has induced the atmospheric carbon dioxide increase. Therefore, although highly suggestive, this graph cannot be used as proof that global warming is a result of increasing atmospheric carbon dioxide. On the other hand, the carbon dioxide increase in the past 100 years is entirely man-made, and the 0.7°C warming observed over the same period is consistent with some predic-

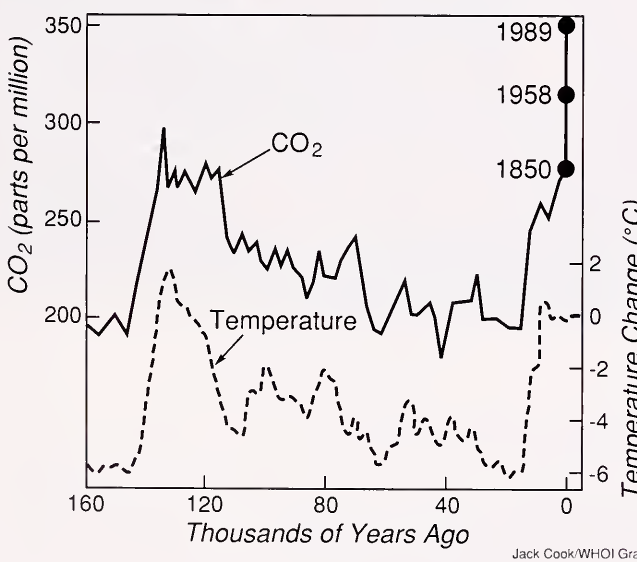
One theory holds that the carbon dioxide released into the atmosphere (as a result of human activities) is trapping the sun's heat, causing the global temperature to rise.

tions based on advanced climate model calculations that include the effects of atmospheric greenhouse gas buildup. Although this supports the theory of global warming due to greenhouse gases in the air as the result of human activity, this amount of warming or cooling has occurred numerous times in Earth's history. So, the recent warming trend may represent an event in natural variability that has nothing to do with human activities. Both believers and skeptics of human-induced global warming will have to wait until new evidence in favor of one view or the other is uncovered.

Changes in temperature and atmospheric carbon dioxide (CO_2) during the past 160,000 years are charted. The temperature record was estimated based on variations in the oxygen-18/oxygen-16 isotope ratio found in Antarctic ice-core samples. Atmospheric CO_2 concentrations were measured in air bubbles trapped in glacial ice. The results were obtained by a French and Soviet scientific team (Lorius et al, Nature, *1990).*

Why is Carbon Dioxide Important?

Our study concerns the fate of industrial carbon dioxide released into the atmosphere. According to global climate model computation results obtained by James Hansen and colleagues (NASA's Goddard Institute for Space Studies, in 1988), about 55 percent of predicted global warming is attributed to carbon dioxide, 20 percent to CFCs, and the remaining 25 percent to methane and nitrous oxide. In the future, CFC emissions will be reduced according to the Montreal International Protocol for CFC production, and the atmospheric concentration of CFCs could be halved in 50 to 80 years. On the other hand, carbon dioxide is produced as a final combustion product of industrial and domestic carbon-containing fuels as well as through cement manufacturing. It is also released into the atmosphere when forests are cut and burned and when organic matter decays. Because carbon-based fuels (including oil, coal, natural gases, and firewood) are so basic to human activities that range from manufacturing and transportation to heating, cooling, and cooking, its consumption is expected to increase as long as the human population continues to increase, regardless of national levels of industrialization and living standards. It is, therefore, important to understand what controls the rate of carbon dioxide accumulation in the atmosphere.



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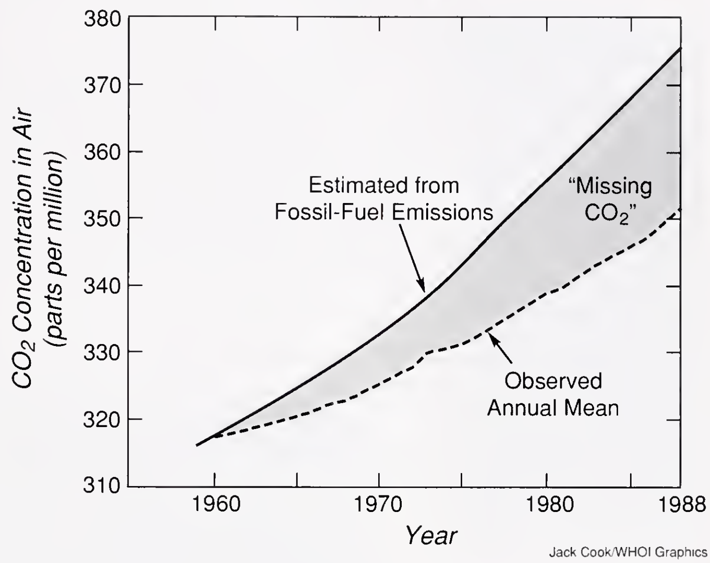
The observed rate of atmospheric increase is about half of the industrial carbon dioxide emission rate. This indicates that about half of the industrial carbon dioxide released into air has been absorbed by natural reservoirs, most likely the oceans and land biosphere, which includes plants, trees, and organics in soil. In other words, carbon dioxide accumulation in the air, and hence possible carbon dioxide-induced global warming, has been somewhat alleviated by the partial disappearance of industrial carbon dioxide.

Two important questions may be asked. The first is "Where does the missing carbon dioxide go?" The answer will help us formulate strategies for alleviating or slowing the carbon dioxide accumulation rate in

air. For example, if the forests are found to be a major sink (absorber) for industrial carbon dioxide, ongoing deforestation must be strongly discouraged or prevented, and tree planting should be encouraged. The second question is "What would happen to the missing carbon dioxide if the climate became warmer?" If the proportion of missing carbon dioxide decreases in response to global warming, industrial carbon dioxide would accumulate in the air at a faster rate. This is a positive-feedback condition that could lead to a faster rate of global warming, and hence to global disaster. On the other hand, if warming causes carbon reservoirs to absorb more carbon dioxide (for example, by more rapid growth of plants), then carbon dioxide-induced warming would cause a reduction in the carbon dioxide accumulation rate in the atmosphere, thus slowing down the warming trend. Eventually, this warming trend would settle down to a certain level due to this negative feedback process. Both scenarios are possible. Here we will address the first question. Although the second question is both relevant and challenging, the answer can only come in the future with diligent, long-term observations and research.



If all industrial emissions stayed in the atmosphere, we would expect the upper curve to reflect atmospheric CO_2 concentrations. The difference between this estimated amount and the mean annual atmospheric CO_2 concentration that has been measured (by C.D. Keeling of Scripps Institution of Oceanography) indicates the amount of "missing CO_2." For 1958, expected and observed values are assumed to be the same.

Early Estimates for Oceanic Uptake of Industrial Carbon Dioxide

Atmospheric carbon dioxide concentration is regulated by a dynamic balance between carbon dioxide supply and demand by carbon reservoirs. The oceans and land biosphere are two major reservoirs exchanging carbon dioxide with the atmosphere at a significant rate. Hans Oeschger, Uli Siegenthaler, and their colleagues (University of Bern, Switzerland), and Wally Broecker (Lamont-Doherty Geological Observatory of Columbia University), and Tsung-hung Peng (Oak Ridge National Laboratory), among others, formulated computer models to simulate industrial carbon dioxide uptake by an idealized atmosphere and ocean. The world ocean was represented by a two-layer box of water with a 75-meter-thick surface layer and a 4,000-meter-thick deep layer. The atmosphere was represented by a single homogeneous body that exchanged carbon dioxide across the sea surface.

According to the models, the carbon dioxide gas entered the surface layer and diffused into the deep layer. Rates of carbon dioxide movements were estimated using the measured distribution of natural radioactive carbon-14 in the air and oceans. Since carbon-14 atoms are in the form of carbon dioxide molecules, their distribution should closely approximate the uptake and spreading of industrial carbon dioxide in the oceans. As observed in ice cores, the pre-industrial carbon dioxide concentration in the atmosphere was steady at about 280 parts per

North Pole air contains, on average, about 3 parts per million more carbon dioxide than South Pole air.

million, so the researchers considered that carbon dioxide sources and sinks were balanced then. In addition, they assumed that atmospheric carbon dioxide was in equilibrium with the surface-water layer in 1850. To this initial condition, industrial carbon dioxide was added to the atmospheric box at rates closely approximating actual industrial records. Because the annual effect of industrial carbon dioxide was small, it was treated in the model as a perturbation, and the biological effect on the carbon cycle in the oceans was assumed to be unchanged.

Their results show that 30 to 35 percent of industrial carbon dioxide should be taken up by oceans, 15 to 20 percent should be taken up by the land biosphere, and the remaining 50 percent should remain in the atmosphere. Hence the oceans are the most important sink for industrial carbon dioxide. More recent studies by Jorge Sarmiento (Princeton University) and his associates at the Geophysical Fluid Dynamics Laboratory of the National Oceanic and Atmospheric Administration (NOAA) employ an advanced three-dimensional ocean circulation model instead of the highly idealized one-dimensional ocean models used for the earlier studies. However, they assumed that the surface layers of pre-industrial oceans were initially in equilibrium with atmospheric carbon dioxide everywhere in the world, and treated the industrial effect as a perturbation. As we will show, this assumption is inconsistent with observations. Their estimates of carbon dioxide uptake are similar to those of the earlier studies based upon idealized oceans.

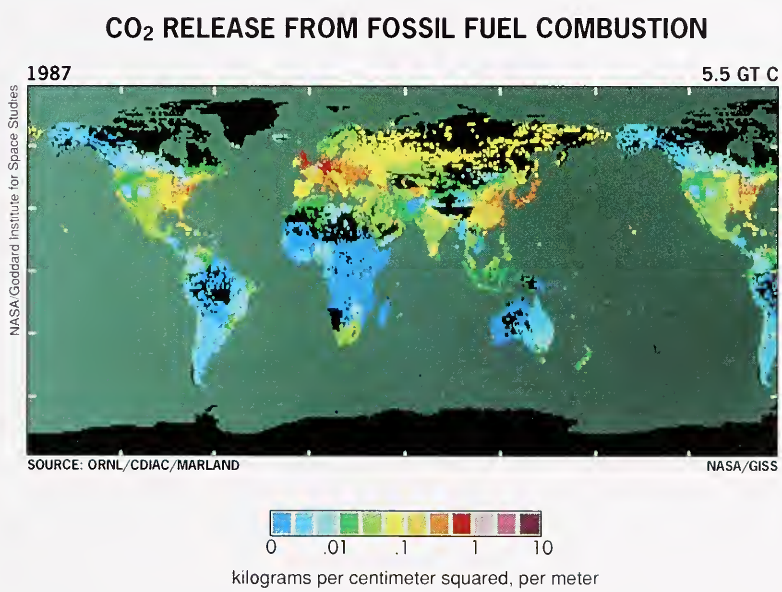
A New Approach

Our basic premise is that carbon dioxide concentration in a given atmospheric position is governed by the transport of carbon dioxide in the air by wind and other air motions as well as by the geographic and temporal patterns of carbon dioxide sinks and sources. The carbon dioxide distribution in air has been measured at many locations on Earth, and the location and intensity of industrial sources have been estimated from energy consumption statistics. The oceanic carbon dioxide sinks and sources over the Northern Hemisphere and equatorial oceans have been measured aboard research vessels and commercial ships. However, the distribution and intensity of carbon dioxide sinks and sources over the land biosphere are poorly known, as are those over the Southern Hemisphere oceans, especially during the winter period. We have therefore used the following three sets of known information, in conjunction with the advanced three-dimensional model for global atmospheric circulation, and obtained estimates for the two unknowns: the carbon dioxide sink/source intensities for the land biosphere and the Southern Hemisphere oceans.

North-South Difference in Atmospheric Carbon Dioxide. Accurate monitoring of atmospheric carbon dioxide concentration was started by C.D. Keeling and his associates (Scripps Institution of Oceanography) during the International Geophysical Year in 1957. Their observational data show that during the last decade carbon dioxide concentration has been increasing at a mean rate of about 1.4 parts per million per year. This corresponds to an atmospheric carbon dioxide increase of about 3.0 billion tons as carbon per year during the past several years. Furthermore, based upon measurements obtained between 1981 and 1987 at

some 20 stations located all over the world, the scientists at the Climate Monitoring and Diagnostics Laboratory of NOAA in Boulder, Colorado, demonstrated that annual mean carbon dioxide concentrations in northern air are greater than that of southern air. North Pole air contains, on average, about 3 parts per million more carbon dioxide than South Pole air. This information is very important to our study, since the north-south gradient of the atmospheric carbon dioxide concentration is affected by the distribution of carbon dioxide sinks and sources as well as by the rate of large-scale atmospheric mixing between the Northern and Southern hemispheres.

Industrial Sources of Carbon Dioxide. The industrial carbon dioxide emission rate has been estimated, based on United Nations and other governmental records for fossil-fuels and cement production. However, the global carbon dioxide emission rate cannot be estimated as precisely as desired. For example, coal is a major fossil fuel, produced and consumed in Eastern European countries and the Peoples Republic of China.



As the colors indicate, industrial CO_2 sources are unevenly distributed throughout the world. The US is responsible for the highest level of CO_2 emissions (22 percent) followed by the former USSR region (18 percent), the Peoples Republic of China (10 percent), Japan (5 percent), Germany (4.5 percent), India (3 percent), and the UK (2.6 percent). The remaining 34.9 percent is distributed throughout other regions. (Courtesy of G. Marland, Oak Ridge National Laboratory.)

Together these countries are responsible for more than 30 percent of the world's industrial carbon dioxide emissions, while the US emits 22 percent. However, since their carbon contents or BTU (British thermal units) are poorly known, carbon dioxide emissions cannot be reliably computed based on the production tonnage of coal.

Gregg Marland (Oak Ridge National Laboratories) places the uncertainty of global carbon dioxide emissions (such as the ones shown on page 21) to about 13 percent. Based on the information provided by Marland, we estimate that the mean annual industrial carbon dioxide emission rate from 1981 to 1987 was 5.3 billion tons (as carbon) per year. The geographical distribution data for the industrial sources have been compiled by Marland, and his data are used in the three-dimensional GISS/NOAA general circulation model of the atmosphere above. About

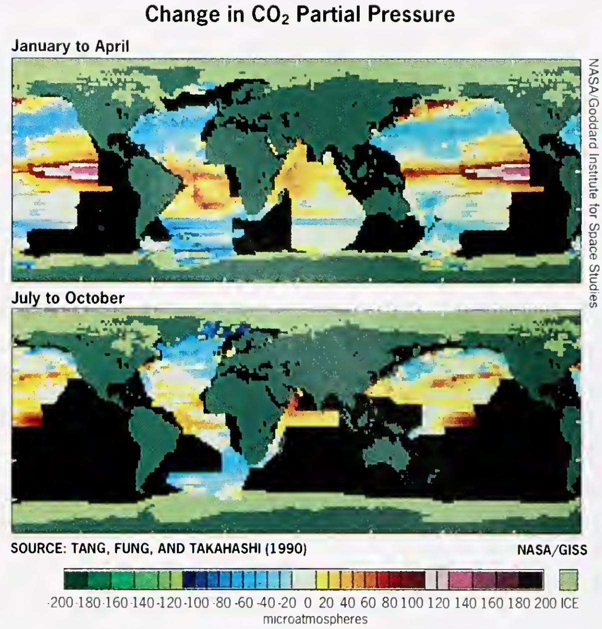
96 percent of the annual emissions are from northern sources.

Oceanic Carbon Dioxide Sinks and Sources. The net carbon dioxide flux across the sea surface may be characterized by the chemical driving force and the gas-transfer rate coefficient. The former is the difference between the partial pressure of carbon dioxide in surface ocean water and that in the overlying air. This tells, like relative humidity, whether water is undersaturated or supersaturated with atmospheric carbon dioxide. The transfer rate is a difficult quantity to measure at sea, and hence is estimated via special laboratory or field experiments. Multiplying these two quantities yields the net carbon dioxide flux across the sea surface.

Generally, warm equatorial waters are strong sources of carbon dioxide to the atmosphere, whereas colder waters are carbon dioxide sinks.

Carbon dioxide partial pressure measurements conducted by scientists at Lamont-Doherty Geological Observatory and NOAA's Pacific Marine Environmental Laboratories in Seattle, Washington, are summarized in the graph opposite.The upper panel represents the 1972 to 1989 mean distribution during the four-month period of January through April, and the lower panel represents that for July through October. Generally, warm equatorial waters, especially those in the Pacific equatorial zone, are a strong source of carbon dioxide to the atmosphere, whereas colder waters in higher latitudes are carbon dioxide sinks. The Pacific equatorial waters are the most important oceanic carbon dioxide source, and are sustained by upwelling of carbon dioxide-rich subsurface waters. Although the seasonal variability of the source intensity is relatively minor (about 25 percent) during the normal, non-El Niño years, this source is eliminated by the blanketing effect of warm, low-carbon dioxide surface water, which spreads eastward from the western Pacific during an El Niño event (see The Interplay of El Niño and La Niña, *Oceanus*, Summer 1989). Such an event is known to occur once every five to seven years.

The map also reveals that a subarctic area in the western North Pacific Ocean is a strong carbon dioxide source during the northern winter, when the water is coldest, but becomes a strong carbon dioxide sink during summer when the water is warmest. Similar seasonal changes have been observed in the Weddell Sea, near Antarctica. During winter, the surface water is chilled and becomes more dense than the underlying deep waters, thus setting off deep convective circulation. This causes nutrient-rich deep waters rich in carbon dioxide (see figure 1 on page 24, *Oceanus*, Summer 1989) to rise to the surface. Accordingly, carbon dioxide trapped in deep water is released to the atmosphere during this deep convection period in winter. In spring and summer, more sunlight becomes available, stimulating rapid phytoplankton growth in surface ocean waters. This growth utilizes carbon dioxide and nutrients that were brought up to surface during the previous winter, and reduces the carbon dioxide partial pressure in the surface water to below the atmospheric level. This occurs despite substantial warming of the water, which by itself causes the carbon dioxide partial pressure in water to increase. Thus, proliferation of photosynthetic plankton in summer is mainly responsible for the ocean becoming a carbon dioxide sink in these high-latitude regions. Biological productivity in the great oceanic gyres at temperate latitudes is very low. As a result, the seasonal changes of the carbon dioxide partial pressure in those regions are driven mainly by seasonal temperature changes.



Using color to depict CO_2 partial pressures (expressed in micro-atmospheres), this map illustrates the observed differences between CO_2 concentrations in the atmosphere and the surface ocean to reveal CO_2 transfer between them. Mean values for normal, non-El Niño years from 1972 to 1989 are presented for two four-month periods, January through April and July through October. The oceanic CO_2 sink areas, where atmospheric CO_2 is taken up by seawater, are shown in blue to green, and oceanic source areas, where surface ocean water is releasing CO_2 into air, are shown in yellow to purple. White indicates areas where no net transfer occurs, and black indicates areas for which we have no measurements during these two seasonal periods.

Across the sea surface, the carbon dioxide gas-transfer coefficient is primarily determined by the degree of turbulence of air above and water below the interface. For practical reasons, it is often expressed as a function of wind speed. At wind speeds below about 3 meters per second, the sea surface is hardly stirred and looks like a mirror. Under these conditions, the carbon dioxide gas exchange rate is very low. At higher wind speeds, the gas is transferred across the sea surface at a higher rate. However, the results of field and laboratory experiments differ by as much as 100 percent. For this discussion, we will use a wind speed dependence that has been estimated on the basis of the air-sea distribution of radioactive carbon-14 produced by natural processes and nuclear-bomb tests (see figure 4 on page 28, *Oceanus*, Summer 1989). Using this relationship in concert with the mean monthly distribution of wind speed over the global oceans and the sea-air carbon dioxide partial pressure difference, the net carbon dioxide flux across the sea surface has been computed. The carbon dioxide values in areas where measurements have not been made were estimated from temperature-carbon dioxide correlations of adjacent areas. In this way, we found that the Pacific, Atlantic, and Indian oceans north of the 15°N parallel together take up about 0.6 billion tons of carbon as carbon dioxide annually, whereas the equatorial belt (15°N to 15°S) of these three oceans releases about 1.3 billion tons of carbon as carbon dioxide during a normal, non-El Niño year. Since equatorial release exceeds northern ocean uptake, balancing the global oceanic carbon dioxide budget hinges upon the sink intensity of the southern oceans.

Atmospheric General Circulation Model. An important computational model ties these observations together. Commonly called a General Circulation Model or GCM, this model mathematically describes large-scale global circulation of the atmosphere, based on a number of physics principles. It has been used to predict global climate changes as well as to study gas dispersion in the atmosphere. The GCM we used was developed by James Hansen and his associates. The earth's surface is divided into boxes, each 4° latitude by 5° longitude [in mid-latitudes, this corresponds to an area about 250 miles (east to west) by 280 miles (north

Reduced atmospheric carbon dioxide in summer indicates that land-plant growth extracts a large quantity of carbon dioxide from air.

to south)], and the atmospheric column above the boxes is divided into nine layers, according to pressure or height above ground level. In each box, energy from the sun is exchanged between the layers via absorption, reflection, and re-remission of light and heat by ground surfaces and clouds, via evaporation, condensation, and precipitation of water (clouds, rain, and snow), and via air motion (winds and turbulence).

The model was fine-tuned by adjusting "eddy mixing" of air in each box, so that observed atmospheric distributions of krypton-85 and CFCs were matched. These man-made gases are ideally suited for testing and calibrating the transport of air in these atmospheric circulation models, since their sources are located in the industrial north like the industrial carbon dioxide sources. Furthermore, they are only sparingly soluble in seawater and are not taken up by land biosphere via photosynthesis. As a final test for the model, seasonal variation of atmospheric carbon dioxide concentration at various altitudes was calculated using satellite-based land photosynthesis and respiration data previously obtained by Fung and her associates in 1987, and compared with observed values over Scandinavia and Australia.The computed results are in good agreement with the observations, giving us confidence in the model.

Using the GCM described, we first determined the effect of industrial carbon dioxide sources alone. A world industrial carbon dioxide emission of 5.3 billion tons of carbon per year was added to the model with the global distribution as illustrated in the figure on page 23. When charted, it is apparent that a strong northern sink is required to reduce carbon dioxide concentrations in northern air and flatten the north-south gradient, thus making the computed and observed curves agree.

Global Carbon Dioxide Budget

The observation that atmospheric carbon dioxide concentration is reduced substantially during summer, particularly in the Northern Hemisphere, indicates that the growth of land plants extracts a large quantity of carbon dioxide from the air even though a portion of the fixed carbon may be returned to the air by plant decay. A survey of New England areas has shown that forests have been recovering from the deforestation inflicted during pioneer days. On the other hand, deforestation is currently in progress in tropical areas of Brazil and Southeast Asia where farmlands and forests are being removed and houses are being built. Because of the highly uneven and diverse distribution of land plants and soil carbon, it is not possible to extrapolate local changes to a global scale. Although satellite surveys show areal changes in land use and vegetation in many regions, they do not give changes in the mass of soil carbon and plant carbon. Accordingly, we have attempted to estimate the amount of carbon dioxide taken up by the land biosphere based on measurements made in the air and oceans.

With our method, we tried to estimate the flux of carbon dioxide uptake by the southern oceans and land biosphere using the atmospheric GCM and available observations. The following quantities are considered known, as discussed earlier:

- global industrial carbon dioxide emissions of 5.3 billion tons of carbon per year, and its distribution,
- mean annual north-south gradient in atmospheric carbon dioxide

concentration (3 parts per million from the North Pole to the South Pole),
- net carbon dioxide sink and source fluxes over the oceanic areas north of 15°S latitude, and their distribution, and
- global forest distribution and relative intensity of photosynthesis and respiration, including that of tropical deforested areas.

Information for global forest distribution was obtained through high-resolution color scanning satellite observations by NOAA. In addition, on the basis of published information, we believe plant growth rates may be enhanced by increased carbon dioxide concentrations in air (called the "carbon dioxide fertilization effect"), up to 5 percent or an additional 3 billion tons of carbon per year, and that tropical deforestation activities annually release 1 to 2.5 billion tons of carbon (as carbon dioxide) into the air. The carbon dioxide uptake rate by the southern oceans and the terrestrial biota have been computed for a variety of realistic scenarios. In all cases, our calculation demands that the amount of carbon dioxide taken up by various reservoirs be balanced with that released from industrial and deforestation activities. Two common features emerge in many cases attempted. First, a strong carbon dioxide sink by temperate forests of 2 to 3 billion tons of carbon per year is needed to account for the observed north-south gradient of atmospheric carbon dioxide. Second, the southern oceans should take up 1 to 1.5 billion tons of carbon annually. This estimate is consistent with the limited number of carbon dioxide measurements made over the southern oceans. This means that global oceanic flux values estimated from measured and computed values combined are less than 1 billion tons of carbon, and are far smaller (one-third or less) than those for global land-biosphere uptake, which ranges between 1.6 and 2.0 billion tons. In contrast with earlier estimates, the major sink for industrial carbon dioxide released into the atmosphere appears to be not the oceans, but the northern forests! This conclusion is not significantly affected, even if much lower values for carbon dioxide gas-exchange rates across the sea surface are used.

In contrast with earlier estimates, the major sink for industrial carbon dioxide released into the atmosphere appears to be not the oceans, but the northern forests!

Qualifying Our Conclusions

Our attempt to obtain an improved carbon cycle inventory using available data for carbon dioxide in the atmosphere and oceans has lead us to conclude that the biospheric uptake of industrial carbon dioxide is significantly greater than the oceanic uptake, and that the northern forests are sequestering a considerable portion of industrial carbon dioxide. If our conclusion is correct, this would have serious implications for national and international energy policies. To alleviate accelerated carbon dioxide accumulation in the atmosphere, increased forest productivity via advanced ecosystem management should be encouraged, in combination with reduced deforestation activities.

However, we feel that our conclusion requires further scrutiny and testing with additional scientific information. Our carbon dioxide inventory computation predicts that 2 to 4 billion tons of carbon should be accumulating in the northern forest ecosystems each year. If carbon is accumulating at this rate evenly over the northern land areas, there would be an increase in carbon standing crop of 25 to 50 grams per square meter each year, or 500 to 1,000 grams of carbon per square meter

(1 to 2 pounds of carbon per square yard) for 25 years. The carbon standing crop is the total amount of all the forms of carbon present over an entire unit area of land, and includes plants, litters, and soil carbon. Since the average standing crop of land biomass is about 13 kilograms per square meter, the predicted increase corresponds to 4 to 8 percent of the standing crop. Therefore, if our estimates are correct, the northern forested areas have gained several percent of carbon standing crops as living trees, litter, and soil carbon. Is it there? Presently, too little information is available to substantiate or refute our conclusion.

To alleviate accelerated carbon dioxide accumulation in the atmosphere, increased forest productivity should be encouraged, in combination with reduced deforestation activities.

Our conclusion may be also tested using changes in the stable-carbon isotope ratio, carbon-13/carbon-12, in atmospheric carbon dioxide. Since the carbon atoms released from fossil fuels are depleted in the heavier isotope, carbon-13, by about 2 percent, compared with those in atmospheric carbon dioxide, the emission of fossil-fuel carbon would make atmospheric carbon isotopically lighter. This effect is counteracted by photosynthetic utilization of carbon dioxide by land plants, which would preferentially take up lighter carbon-12 and thus cause the remaining atmospheric carbon dioxide to become heavier. Although the carbon isotope ratio in air is thus partially controlled by these two processes, its space and time variation is also affected by the carbon dioxide exchange of both isotopes with the oceans. Therefore, observed changes in the carbon isotope ratio in atmospheric carbon dioxide are not large, but could yield information on biological carbon dioxide sinks. However, the resulting estimates are sensitive to the difference between the isotopic ratio for current photosynthetic carbon fixation and that in carbon dioxide released by the decomposition of older organic debris in the biosphere. Continued investigations of the carbon isotope ratio should yield independent information on the fate of industrial carbon dioxide in the future.

Taro Takahashi is a marine geochemist and Associate Director of the Lamont-Doherty Geological Observatory of Columbia University. Since the International Geophysical Year, 1957 to 1959, he has been engaged in a global study of carbon dioxide in the oceans. In 1958, he discovered a solitary seamount in the eastern South Atlantic Ocean and named it the Vema Seamount. He is Chairman of the Ocean Carbon Dioxide Committee, National Research Council.

Pieter P. Tans is a physicist working at the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration in Boulder, Colorado. Since his graduate-student days in the Netherlands, he has been interested in man's impact on the global climate and in greenhouse gases in the atmosphere and oceans. He has also probed the behavior of air and water as a small-sailboat racer.

Inez Fung is an atmospheric physicist at the NASA Goddard Institute for Space Studies in New York City. Her current activities in carbon-cycle modeling and climate modeling grew out of seeds planted during her undergraduate and graduate studies. In 1989 she was awarded NASA's Exceptional Scientific Achievement Medal.

Biomedical Uses for Natural Marine Chemicals

D. John Faulkner

The earliest recorded use of marine life as a chemical source dates back many centuries. Ancient Phoenicians employed a chemical secretion from marine molluscs to produce "Tyrian" or "Royal" purple dyes for woolen cloth. Using marine organisms to procure chemicals on a commercial scale is rare, however. In the past, iodine and bromine were gleaned from seaweeds, and in some coastal communities, seaweeds cast ashore in storms were spread over fields to fertilize the soil. [Still are in northeastern gardens.—Ed.] Currently, selected seaweeds are commercially harvested to obtain industrial products such as agar, alginic acid, carrageenan, and ß-carotene. Only during the last two decades have scientists undertaken a systematic, worldwide search for commercially valuable chemicals from marine organisms. Only a small proportion of these organisms has been investigated so far, but this research has already resulted in discoveries that benefit the biomedical sciences.

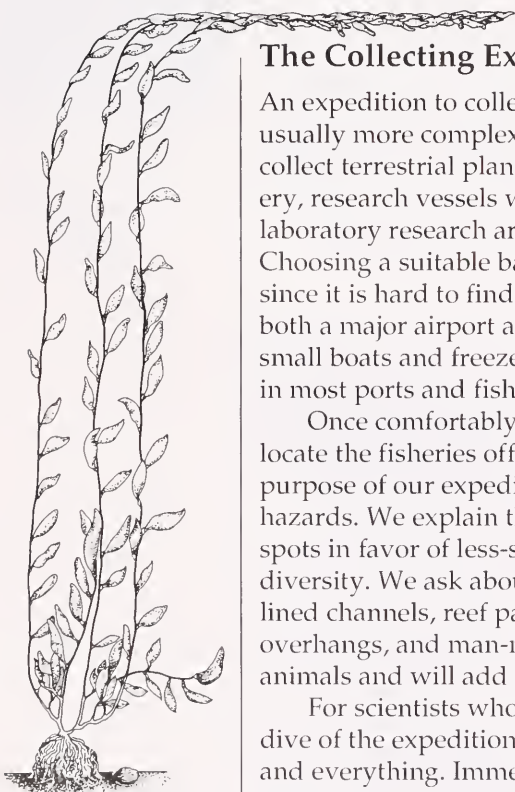
Editor's note: In response to the author's plea, "Please don't change mollusc to mollusk: the incorrect spelling is due to ignorant New Englanders who were involved in the kommercial exploitation of krabs and klams," we say, "Good argument. You win."

Although I focus here on biomedical uses of chemicals from marine sources, the valuable industrial products from seaweeds cannot be ignored. Presently the only marine organisms consistently harvested for their chemical contents are the fast-growing marine algae. Along the coasts of California and Mexico, the giant kelp *Macrocystis pyrifera* is periodically harvested as raw material to make alginic acid, a polysaccharide (a large polymer made up of sugar units) that is modified to make emulsifiers for foodstuffs, pharmaceuticals, and cosmetics. One alginic acid derivative is, for example, added to beer to give it a long-lasting head of foam. Several red algae, particularly those of the family Gigartinales, are harvested to produce the food additives agar and carrageenan. Agar is also used as a growth medium for bacteria in the laboratory. Other marine organisms can also be used as biopolymer sources. Discarded crustacean shells are processed to yield chitin, a celluloselike polysaccharide. The orange pigment ß-carotene, which is used to color food, is produced from the microalga *Dunalliela salina* that is grown in brackish ponds in Australia, Israel, China, and other Asian countries. This may seem like a very small number of industrial products from so rich an environment, but to me it simply reflects the inherent difficulty of exploiting the marine ecosystem.

Natural Drug Sources

The most valuable chemicals that can be acquired from natural sources are those used to treat illness. Many frequently prescribed medicines are naturally existing chemicals, known as natural products, that are obtained from terrestrial plants or micro-organisms that can be grown on an industrial scale. Some well-known examples are the antimalarial drug quinine, which is obtained from fever-tree (*Cinchona officinalis*) bark, the analgesics codeine and morphine from opium-poppy (*Papaver somniferum*) latex, the cardiac glycoside digitoxin from foxglove (*Digitalis purpurea*), and antibiotics such as the penicillins, tetracyclines, and cephalosporins, which are produced by microbial fermentation. Natural products from plants are often the cheapest and most effective drugs available, particularly in the Third World, and they come to us as a legacy of folk medicine based on herbal remedies.

Unfortunately, we have no such legacy for the marine environment. Until the development of scuba, it was impossible to explore the undersea world, and even the intertidal zone was largely ignored because it was a dangerous environment. Yet the diversity of marine plants and invertebrates far exceeds that found on land. On a purely statistical basis, we could expect many useful chemicals to be found in marine organisms; however, we must also expect them to be difficult to acquire.



E Paul Oberlander/WHOI Graphics

The giant kelp, Macrocystis pyrifera.

The Collecting Expedition

An expedition to collect marine specimens for biomedical research is usually more complex and demanding than a similar expedition to collect terrestrial plant materials. Despite the importance of drug discovery, research vessels with facilities to support diving operations and laboratory research are seldom available to researchers in this field. Choosing a suitable base for a collecting expedition is most important, since it is hard to find a marine laboratory or dive shop that is close to both a major airport and relatively unspoiled environments. Access to small boats and freezer facilities is also essential, but these are available in most ports and fishing communities.

Once comfortably established at a home base, the first task is to locate the fisheries officer or other local experts to communicate the purpose of our expedition and garner their advice concerning local hazards. We explain that we want to avoid the choice tourist diving spots in favor of less-spectacular locations of equal or greater biological diversity. We ask about unique microenvironments such as mangrove-lined channels, reef passes, shallow lagoons, underwater caves and overhangs, and man-made structures, all of which harbor a variety of animals and will add to the richness of our collection.

For scientists who spend most of their days in a laboratory, the first dive of the expedition is so exciting that they collect a little of anything and everything. Immediately after the dive, samples are pooled and sorted, and each specimen is numbered, classified, recorded in field notebooks, photographed, and then placed in plastic bags or jars and frozen. This usually takes far longer than the dive, and invariably results in vows to take fewer, but better, samples in the days ahead. Before long the divers notice that some invertebrates attached to the reef, such as

sponges, soft corals, and tunicates, appear to repel their neighbors, and that these and certain other soft-tissued animals are avoided by fish, crabs, and other predators. Avoidance of soft-bodied animals by potential predators indicates that the animals are probably producing defensive chemicals. These species likely contain biomedically important chemicals, for any chemical that can elicit such a profound ecological response should also have other biochemical and pharmacological properties.

D. John Faulkner

Luffariella variabilis *produces large amounts of manoalide, a chemical that has anti-inflammatory and pain-killing effects. This common, dark-gray sponge is distinguished by the orange fibers, apparent here, that form its internal skeleton.*

The Next Step: Isolating, Purifying, and Identifying Chemicals

The pharmacological screening program is the heart of drug-discovery research. Although some simple bioassays (tests that indicate biological activity) can be performed in the field to guide the collection program, most bioassays used to isolate the chemicals must be performed in well-equipped laboratories. A small portion of each specimen is extracted with a solvent such as ethanol, and this crude extract is a wide assortment of bioassays. These may include:

- *antimicrobial assays* to detect chemicals that inhibit the growth of bacteria, fungi, or viruses,
- *cytotoxicity assays* that measure the ability to selectively inhibit cancer-cell growth,
- *enzyme inhibition assays* such as those used to detect potential anti-inflammatory agents, and/or
- *anti-mitotic assays* that indicate the ability to prevent cell division and, ultimately, cell multiplication.

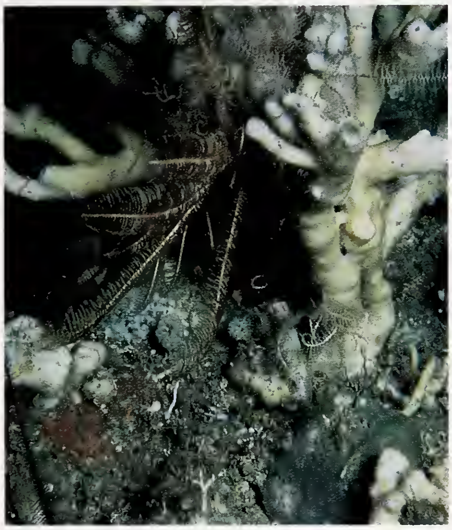
When an extract produces the desired effect in a bioassay, the remainder of that sample is extracted and then separated into its component chemicals. Whenever possible, each step of the purification is guided by bioassay results to obtain pure bioactive chemicals. These are then identified using spectroscopic methods that relate the physical properties of a molecule to its chemical structure. Pure chemicals of established identity that possess desirable pharmacological properties are the leads that the pharmaceutical industry needs to develop new drugs.

Manoalide: A Case History

The discovery of anti-inflammatory agents from marine sponges will serve to illustrate the process of drug development. In 1979, my research group from the Scripps Institution of Oceanography collected marine organisms in Palau, a Pacific island in the Western Caroline group. One of the most abundant invertebrates on the reefs around Koror was a dark-gray encrusting sponge, *Luffariella variabilis*, that could be distinguished by orange fibers that form its internal skeleton. This sponge produces relatively large amounts (about 1 percent of its dry weight) of a

chemical with anti-inflammatory activity that Paul Scheuer (University of Hawaii at Manoa) has named manoalide. As part of a drug-discovery program sponsored by California Sea Grant, we submitted a purified sample of manoalide for pharmacological screening to Robert Jacobs at the University of California, Santa Barbara. Manoalide was analyzed in a variety of assays and was shown to be effective, first as an analgesic (pain killer) and then as an anti-inflammatory agent. In a beautiful piece of detective work, Jacobs and his students performed a series of pharmacological experiments to determine how manoalide acts to reduce pain and inflammation. They found that manoalide inhibits the action of an enzyme called phospholipase A_2. This enzyme is responsible for releasing arachidonic acid, the key chemical involved in the biochemical processes that lead to pain and swelling from arthritis, gout, psoriasis, bee stings, poison oak, and many other inflammatory conditions.

J. Reed



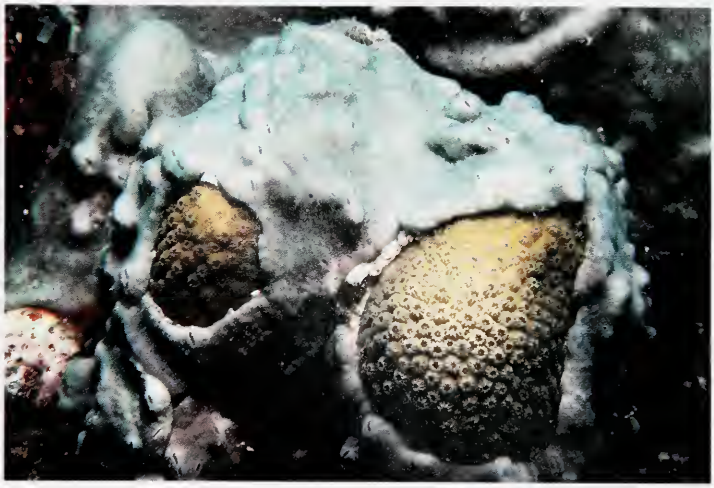
This deep-water sponge, Discodermia *sp., was collected at 500 feet near the Bahamas, where it is commonly found. The powerful immunosuppressive agent discodermolide originates from this organism. (This photo was taken from* Johnson-Sea-Link *submersible of Harbor Branch Oceanographic Institution.)*

Based on this finding, we screened chemicals from many related sponges against phospholipase A_2 (isolated from bee venom), and were pleasantly surprised to find several other anti-inflammatory agents. Our research results encouraged Allergan Pharmaceuticals to begin a development program, eventually resulting in the synthesis of chemicals retaining key features of manoalide but easier to make. Each of these chemical analogues of manoalide were tested in a battery of assays to identify the best candidate for commercial development. Meanwhile, large quantities of manoalide were isolated from the sponge and used to study the pharmacological and toxicological effects of a phospholipase A_2 inhibitor on human and other animal tissues. Although the results were not adequate to allow manoalide to be marketed for topical treatment of psoriasis, they did provide valuable data that will help speed the development of the next generation of synthetic anti-inflammatory drugs. The discovery of manoalide has provided researchers with an important tool to study the role of phospholipase A_2 in inflammation.

Research on manoalide has lasted for 10 years, and the development of a drug based on manoalide will take several years more. Although some may find it disappointing that the marine chemical itself will not be marketed, the drug development program followed a route common in the pharmaceutical industry. We do not expect marine organisms to be harvested as a direct source of pharmaceuticals, except as a last resort. This is because pharmaceutical companies must be able to control all phases of drug manufacture. An oceanic source is well beyond their control.

Many more marine chemicals have excited the interests of the biomedical and pharmaceutical communities. Most of these chemicals are currently regarded as important biochemical probes, meaning they exert profound effects on enzymes, receptor sites, or cellular processes, and can therefore aid in further understanding biochemical processes. Tetrodotoxin, the chemical responsible for puffer fish poisoning, and saxitoxin, the causative agent of paralytic shellfish poisoning, are good examples of marine chemicals that have been used as biochemical

probes. Although both tetrodotoxin and saxitoxin are deadly poisons, they are useful to neurophysiologists studying neuromuscular-transmission mechanisms. Another marine chemical called okadaic acid has become an important tool in studying cellular biochemistry. Okadaic acid was first discovered in a Japanese sponge *Halichondria okadai*, but is now known to be produced by dinoflagellates (microalgae) of the genus *Prorocentrum*.



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Marine Chemicals as Future Pharmaceuticals

Didemnin B, from the tunicate Tridemnum *(above) is being tested as a cancer treatment, and the gorgonian coral* Pseudopterogorgia elisabethae *(below) may provide an anti-inflammatory agent.*

Several marine chemicals are likely candidates for future drugs. Here are a few being explored by US scientists.

- Discodermolide, from the Bahamian sponge *Discodermia dissoluta*, is a powerful immunosuppressive agent that may have a future role in suppressing organ rejection after transplant surgery.
- Bryostatin, from the West Coast bryozoan (moss animal) *Bugula neritina*, and didemnin B, from a Caribbean tunicate of the genus *Trididemnum*, are both in clinical trials as cancer treatments.
- Pseudopterosin E, from the Caribbean gorgonian coral *Pseudopterogorgia elisabethae*, and scalaradial, from dictyoceratid sponges found in the western Pacific, are both being studied as anti-inflammatory agents.

W. Fenical

Other marine chemicals are being investigated in Europe and, most notably, in Japan, but we know less about the progress of these studies. There appears to be no shortage of marine chemicals that are potential candidates for drug development. The problem is that so many chemicals derived from marine organisms show promising activity in the initial screens that it is very difficult to predict which will become truly significant discoveries.

In our search for new drugs, my students and I have been fascinated by the clues that nature provides. For example, the Spanish dancer nudibranch *Hexabranchus sanguineus* (see Creature Feature on page 85) is a large, beautiful marine mollusc whose flowerlike egg masses look good enough to eat. But fishes do not eat the egg masses, and the seemingly defenseless nudibranchs are seldom (if ever) attacked by predators. We discovered that this

nudibranch avoids predation by feeding on chemically protected sponges, and then using the sponge chemicals, known collectively as the halichondramides, for their own defense. The halichondramides are exuded in a mucus secretion when the nudibranch is threatened, and are also incorporated into their egg ribbons to make them distasteful. The nudibranch even performs a simple reaction on the halichondramides to make a more distasteful brew. In addition to being distasteful at low concentrations and toxic at higher levels, the halichondramides are powerful antifungal agents, being as effective as amphotericin B, which physicians use to treat the most serious of fungal infections. They are also potential antitumor agents. The halichondramides do not, however, appear to offer any advantages over proven drugs, so they are not candidates for commercial development. Had they been discovered before amphotericin B, the story might have been quite different.

It seems inevitable that economic considerations will prevent the development of many marine chemicals that are very effective but difficult to obtain. The rise and fall of interest in marine prostanoids clearly illustrates the role of economic forces. Prostaglandins are important human hormones that control blood pressure, renal blood flow, contractions of smooth muscle, and gastric acid secretion, and are involved in inflammation. When prostaglandins were first isolated from sheep seminal tissues, these rare chemicals, badly needed for biomedical research, were difficult to obtain in even minute quantities and hence were extremely expensive. When closely related chemicals called prostanoids were acquired in substantial quantities from the Caribbean

At home in the Caribbean, Plexaura homomalla *(the elongated green coral at center back and right), is relatively safe from commercial harvesters now that prostaglandins are artificially—and inexpensively—produced.*


Jeremy Stafford-Deitsch

gorgonian coral *Plexaura homomalla*, there was a rush to harvest gorgonians, isolate the prostanoids, and convert these chemicals into biochemically active prostaglandins. Within a year, however, prostaglandins were being produced by laboratory synthesis, and the marine prostanoids were soon forgotten, much to the relief of those who value the shallow reef environment's natural beauty. This episode provided a valuable lesson for entrepreneurs seeking new pharmaceuticals from marine organisms: We should expect marine chemicals to inspire new drugs rather than to provide them.

In 1979, I expressed cautious optimism that the decade of the 1980s would lead to important discoveries in the marine pharmacology field (see The Search for Drugs from the Sea, *Oceanus*, Summer 1979). As a participant in this research, I am more than satisfied with progress in this field. Chemicals obtained from marine organisms have proved to be different from those acquired from plant sources, and have provided valuable tools for biomedical research, as well as inspiration to the pharmaceutical industry. Biochemical studies have positively influenced marine biology, in as much as they have focused attention on marine invertebrates and led to pioneering research on invertebrate aquaculture and invertebrate-cell tissue culture. If we consider the 1980s to be a period of basic research on chemicals from marine organisms, then the 1990s will surely see new drugs and other chemical products that were inspired by this research. We will then have accomplished our goal of demonstrating the biomedical potential of chemicals from marine organisms without causing any lasting damage to the marine environment.

We should expect marine chemicals to inspire new drugs rather than to provide them.

D. John Faulkner is Professor of Marine Chemistry at the Scripps Institution of Oceanography, University of California at San Diego. He was trained as an organic chemist but changed his interests to marine natural product chemistry in response to his colleagues' demands. While recognizing that research on pharmaceuticals from marine organisms pays most of the bills, he is very interested in the ecological roles of the chemicals produced by marine plants and animals.

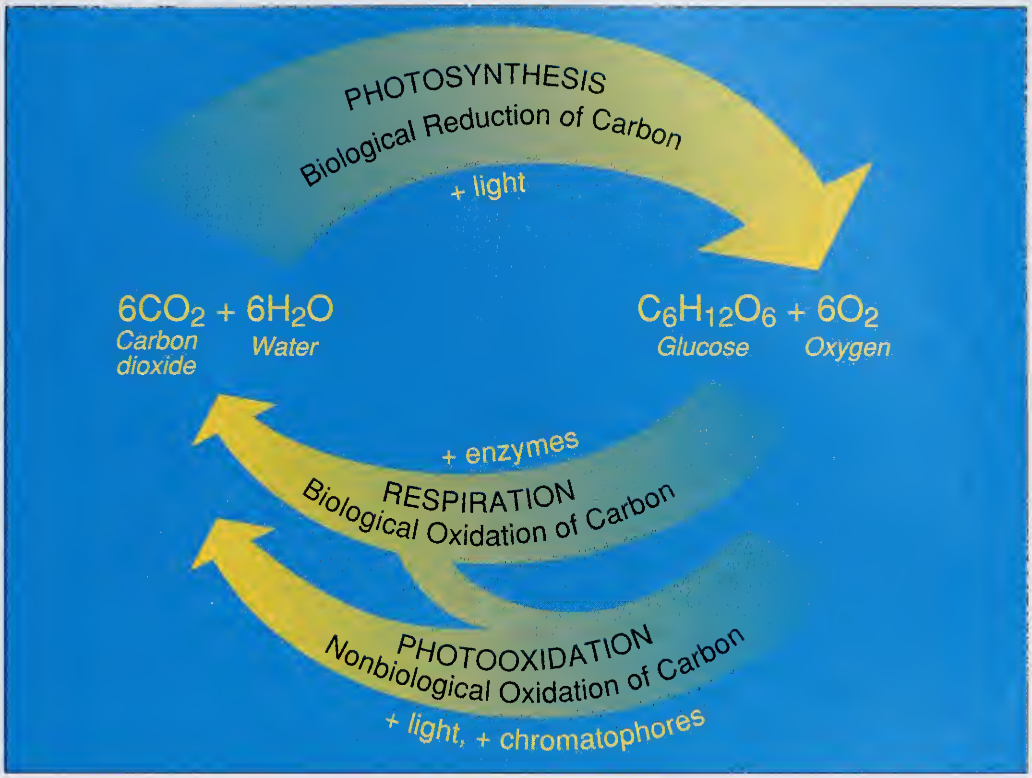
PHOTOCHEMISTRY IN THE OCEANS

SUNLIGHT DRIVES the wind and waves, and is the ultimate energy source for the preponderance of life on Earth. Most people are aware of the importance of phytoplankton in the global oceans. These organisms, employing pigments such as chlorophyll, capture sunlight and convert its energy into chemical forms through the reduction or "fixation" of carbon dioxide. This complex photochemical process, known as photosynthesis, is fundamental to the survival of all but very few organisms. Nonphotosynthetic organisms consume phytoplankton, and use the oxygen released by the photosynthetic process to oxidize the reduced organic compounds, thereby acquiring energy for their growth and maintenance. Known as respiration, this nonphotochemical process depends on the fact that reduced organic compounds and oxygen don't usually react rapidly, but instead require the intermediacy of enzymes within the organisms to catalyze or encourage the oxidative reactions.

However, sunlight captured by certain organic (and inorganic) compounds called chromophores can accelerate these oxidative reactions. By absorbing light, chromophores are activated to an excited state, leading to the formation of transient intermediates that can react rapidly with oxygen. The reaction of oxygen with these intermediates produces a secondary array of highly reactive oxygen species that ultimately gives rise to oxidized products. This nonbiological photochemical process, called photooxidation, is a possible additional route for recycling photosynthetically produced organic compounds.

How important is photooxidation to the recycling of organic matter in sunlit ocean waters? Evidence accumulated over the past decade has provided an increasingly stronger case for the significance of this pathway in the oceanic carbon cycle. This process may control the levels of some organic substances that normally are rather inert to biological oxidation via respiration; indeed, it may be an important initial step in the removal of a significant fraction of oceanic organics. Experimental evidence for this pathway includes the light-dependent production of hydro-

NEIL V. BLOUGH



The biological reduction of carbon, photosynthesis, is balanced by the biological oxidation of carbon, respiration. Another process, the nonbiological oxidation of carbon, or photooxidation, is another possible pathway for recycling the products of photosynthesis. Photooxidation may operate on its own, or it may produce intermediates that then complete the respiration pathway.

gen peroxide, trace gases such as carbon monoxide and carbonyl sulfide, and a variety of small organic compounds, as well as the destruction of chromophores as evidenced by the loss of light absorption. Many of the transient intermediates predicted for this process have recently been identified. Future measurements of the fluxes of these intermediates should provide much better estimates for photooxidation rates on both regional and global scales.

Woods Hole Oceanographic Institution

Marine Organic Geochemistry

Window to the Past

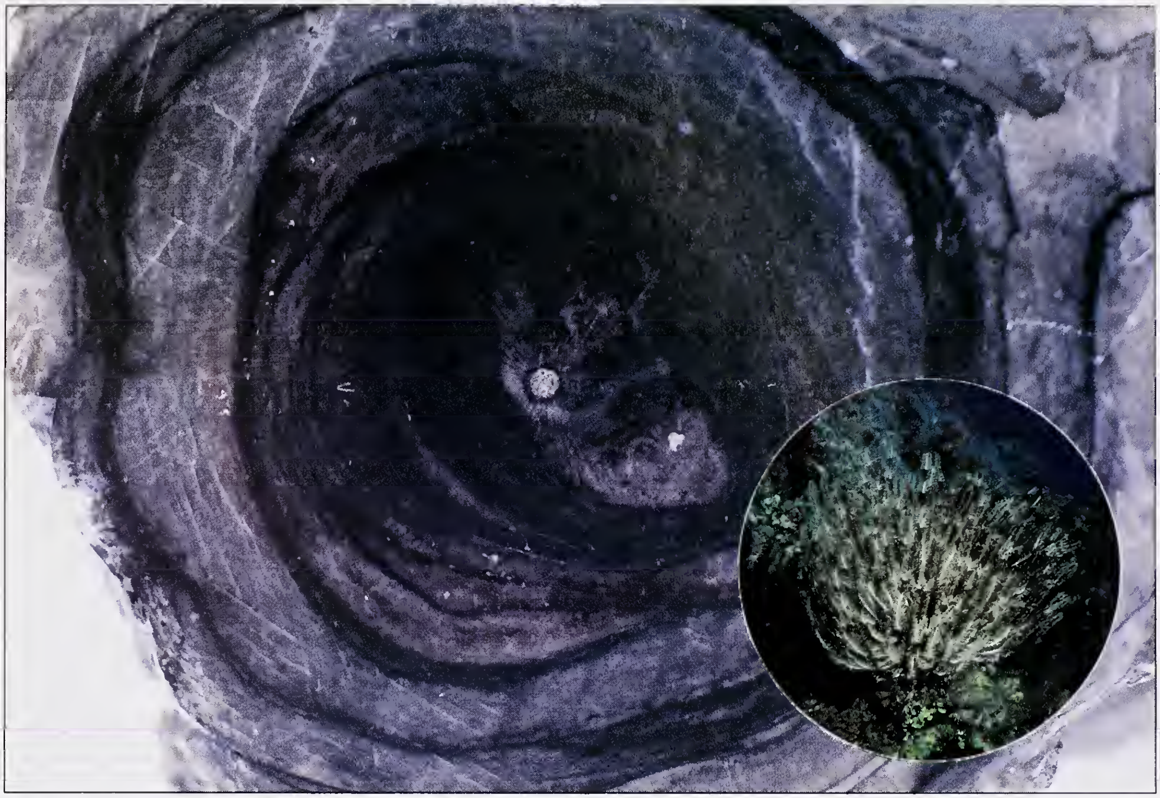
Daniel J. Repeta, Geoffrey Eglinton, and Cindy Lee

The same scientific concepts used to look backward in time through the geological record can be used to follow processes occurring now in the environment.

Organic compounds found in the sea reveal much about Earth's history and the evolution of life. For several decades, oceanographers and organic geochemists have traced "chemical fossils" of early life-forms through the geological record to the organic compounds we find in modern living plants. For example, petroleum is the product of heat and pressure on the remains of marine algae that lived in the sea millions of years ago. One of the first significant studies in the field of organic geochemistry was made in the 1930s by Alfred Treibs, in Germany. He found that petroleum contains porphyrins, a class of organic compounds whose chemical structure closely resembles that of chlorophyll, a pigment found in many living plants. From this, Treibs deduced that oil is formed by heating the remains of ancient plants and animals for millions of years. Treibs's discovery was important: It suggested that oil had a biological—rather than a purely geochemical—origin, and launched a new field of geochemistry called organic geochemistry, in which scientists study organic compounds in the environment at the molecular and elemental levels.

For many years, the search for petroleum dominated the field of organic geochemistry. Petroleum is a very complicated mixture, containing perhaps hundreds of thousands of different organic compounds. The organic structure of molecules from ancient marine algae is preserved in petroleum's components. These "biomarkers" help us follow the intricate paths of changes that occur during the generation of petroleum. Understanding the conditions under which petroleum forms helps exploration geologists find new oil fields.

In recent years, the field of organic geochemistry has expanded greatly. Although tracing the origins of gas and oil is still an integral part of the science, much of the current research focuses on modern systems. The same scientific concepts used to look backward in time through the geological record and study the origin of petroleum can be used to follow chemical, biological, and geological processes occurring now in the environment. One area of interest to today's geochemists is the global carbon cycle, born of concern over the potential for atmospheric warming due to increased greenhouse gas concentrations (see Balancing the Budget, page 18).



Dan Repeta/Phillip S. Lobel (inset)

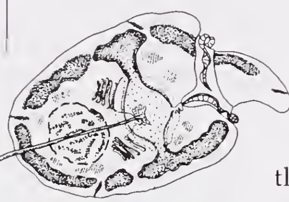
This cross section of a fossilized sea lily (or crinoid) is inset with a modern, living crinoid. The brilliant colors are produced by fossilized remains of pigments that were present in the organism when it lived during the Jurassic Age, some 160 million years ago. This specimen was analyzed by Max Blumer at the University of Basel, Switzerland, in the early 1950s. It was an interest in comparing the organic compounds in fossils such as this with living crinoids that led Blumer to come to Woods Hole Oceanographic Institution (WHOI) in the early 1960s to study organic compounds in the contemporary environment. Blumer's research started a now 30-year tradition of marine organic geochemical research at WHOI.

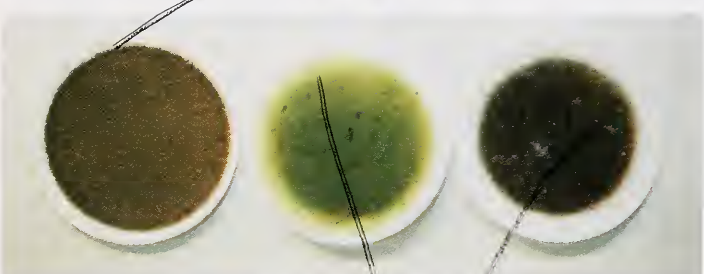
How Do Global Changes Affect the Carbon Cycle?

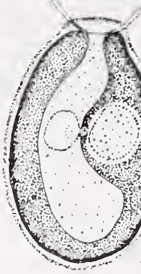
The carbon cycle describes how carbon, in both its organic and inorganic forms, passes through biological and geological reservoirs. Carbon dioxide (CO_2) in the atmosphere is removed by terrestrial plants and marine algae, and converted to organic compounds. On land, much of the carbon is seasonally recycled in deciduous plant leaves, and terrestrial plants may store carbon for much longer times, for example, as wood, or in tropical rain forests where trees and plants do not lose their foliage in autumn. In the sea, organic compounds are manufactured from carbon dioxide by phytoplankton, single-celled, microscopic algae living near the sea surface. Phytoplankton grow in the sunlit upper 150 meters of the world's oceans, using up nutrients and carbon dioxide to make organic compounds and calcium carbonate. Most phytoplankton cells are eaten by zooplankton, whose fecal pellets rapidly fall through abyssal depths to the seafloor, where they provide food for bacteria and benthic organisms. Eventually, as sediment continues to rain down year by year, a tiny fraction of the algal production is buried, out of reach of

benthic feeders and most bacterial attack. This buried carbon enters the sedimentary record. Each layer of sediment on the seafloor contains the remains of algae that lived when the sediment was deposited, thereby preserving a history of environmental conditions. If we know how the carbon cycle has responded to past changes, for example, glacial events, we may be able to make credible predictions for the future.

To fully understand the carbon cycle, we must first understand our present world. Here we will use two examples from our research to illustrate how organic geochemists use the distribution and characteristic structures of organic compounds to study several biological and geological processes. The first involves using pigments to follow the complicated seasonal succession of algal species in the sea, and to determine how this succession can affect ocean chemistry. The second example illustrates how marine algae synthesize organic compounds called alkenones that record the temperature of the algae's ocean habitat. The algae's remains in sediments form an historical record of ocean temperature changes. We can use the record of alkenones deposited up to hundreds of thousands of years ago to decipher changes in Earth's temperature history.





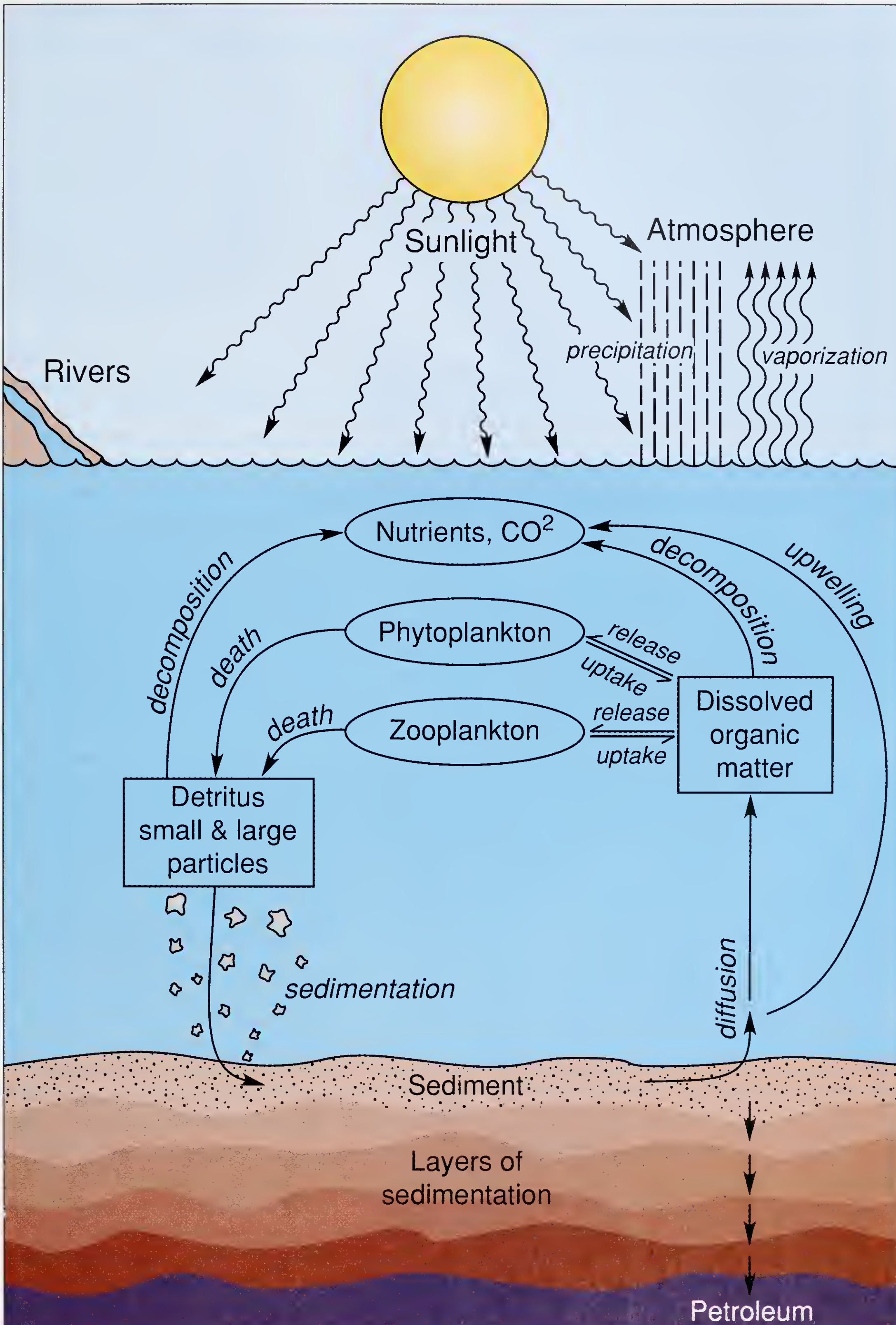


Just as terrestrial plants have distinctive colors, marine algae have colors, too. When seawater is passed through filters, the algae collected on the filter imparts it with a distinctive hue. These filters contain three different algae, the dinoflagellate Amphidinium *(left dish, upper drawing), the green algae* Dunaliella *(center dish, lower drawing), and the prymnesiophyte* Emiliana *(shown on page 43). Each of these three species have different mixtures of chlorophylls and carotenoids, and hence appear in different shades of brown, green, and red.*

Ocean Color: Pigments as Phytoplankton Biomarkers

All marine phytoplankton synthesize highly colored pigments as part of their photosynthetic apparatus. Pigments capture solar energy in the form of visible light and transform it into the chemical energy all organisms need to live. Light absorption gives plant pigments the brilliant greens, reds, yellows, and oranges we associate with trees, flowers, fruits, and vegetables, or in the case of marine algae, with the highly colored algal blooms that frequently appear in coastal ponds and marshes. Chemically, algal pigments fall into two broad categories: the deep-green chlorophylls that give trees and grasses their distinctive hues, and the red-to yellow carotenoids, most familiar to us as the pigments of flowers, fruits, and vegetables. Both pigments are necessary for photosynthesis. When we analyze marine algae samples and separate the pigment mixtures into components, we find that each class of algae contains very specific characteristic pigments. Pigments from several hundred different species of algae, representing all major algal classes found in the ocean today, have been analyzed. Comparing pigment compositions of two algae, *Dunaliella* and *Amphidinium*, shows that although both species contain chlorophylls and carotenoids, the number and type of pigments in each alga are different.

Only about a dozen different chlorophylls are synthesized by marine algae, and one type, chlorophyll-*a*, predominates. Both *Dunaliella* and *Amphidinium* have high concentrations of chlorophyll-*a*. Each algal cell



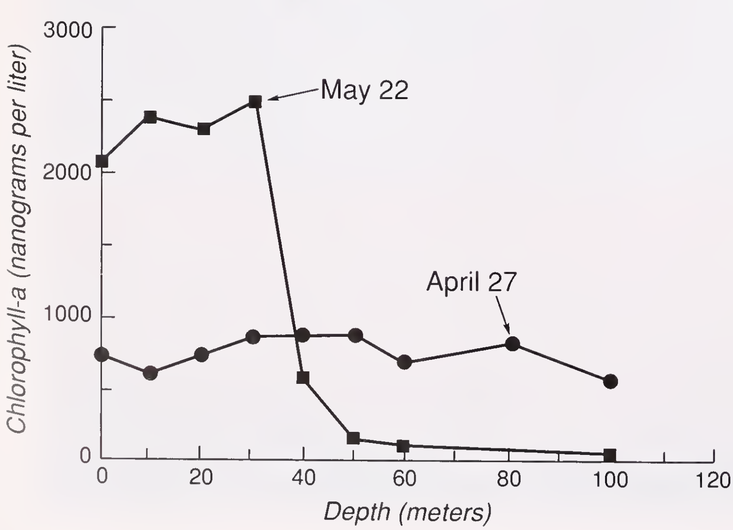
Jack Cook/WHOI Graphics

Changes in physical oceanography stimulate changes in marine biology that influence ocean chemistry. As cold winter storms in the North Atlantic subside in March and April, the ocean warms and a spring phytoplankton bloom occurs. Here are two profiles of chlorophyll-a. The first was collected on April 27 when the water column was well mixed and phytoplankton populations were relatively low. The second profile was collected a month later, when the water column stratified due to solar warming of the surface water. An algal bloom is under way. After the algal bloom peaks, nutrients become exhausted. Chlorophyll values fall but remain concentrated near the surface until new winter storms begin the cycle once again.

must synthesize enough chlorophyll-*a* to harvest all the solar energy it requires to manufacture the organic compounds it needs to live and grow. This fact can help us estimate the distribution, biomass, and annual production of algae in the ocean. By estimating the amount of chlorophyll produced by each cell, we can calculate the total number and mass of cells in a sample from the sample's chlorophyll content. Oceanographers make tens of thousands of such measurements in the world's major ocean basins annually. Over the last two decades, shipboard chlorophyll sampling has been supplemented by satellite measurements made over much larger areas of the sea. The absorption of sunlight by chlorophyll in the upper ocean can be detected by spectral radiometers (which measure solar radiation reflected back to space) mounted on orbiting platforms. By calibrating the remote-sensor data with shipboard chlorophyll analyses, we can quantitatively measure chlorophyll on a much larger portion of the ocean than is possible using shipboard measurements alone, and construct global maps of chlorophyll concentration.

Carotenoids are chemically much more diverse than chlorophylls, and several hundred different carotenoids have been isolated. Many carotenoids are specific to individual algal species, so that carotenoid distribution can be thought of as an algal type's "fingerprint" or signature characteristic, as revealed by orange and yellow bands distributed on chromatography plates. The two algae have the same green-colored bands from chlorophyll; however, their carotenoid distributions are quite different. By analyzing carotenoids in seawater or sediments, we can often identify which algae are present—information that is important to understanding how physical processes are coupled with biological production and chemical cycling of the elements. The following details how we study biogeochemical cycling in the water column, using the distribution of pigments and chemical properties in the eastern North Atlantic Ocean from spring 1989. This study was part of the Joint Global Ocean Flux Program, an international program to investigate the ocean's elemental fluxes (see JGOFS, page 57).

Like most ocean basins, the eastern North Atlantic is characterized by high phytoplankton concentrations in the upper water column. Since pigments serve to collect solar energy, phytoplankton can only survive in a thin layer of seawater that extends from the sea surface to a depth of about 150 meters. At depths greater than 150 meters, there is not enough sunlight to sustain photosynthesis, and the pigment and algae distributions decrease sharply. Each year from November to April, the eastern North Atlantic is buffeted by high winds and cold temperatures that mix the surface ocean to depths in excess of 500 meters. This deep winter mixing homogenizes the water column and transports



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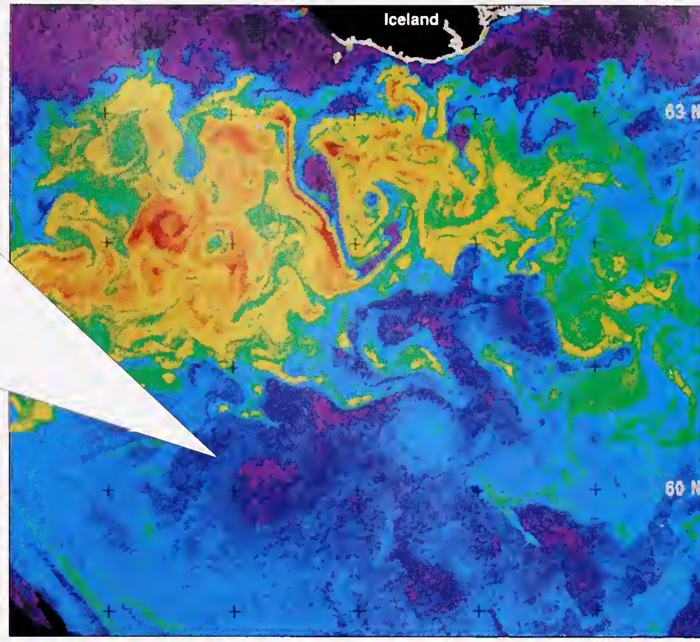


NASA Goddard Space Flight Center/D. Harbour (micrograph)

This spring bloom of the microscopic algae Emiliana huxleyi *(shown in the electron micrograph) occurred in the northeast Atlantic Ocean near Iceland in June 1991. Blooms like this one appear on satellite images virtually every year at about the same time and in the same place. From space, the minute white calcium carbonate shells (coccoliths) of the algae* E. huxleyi *show up as milky white spirals and swirls many kilometers across, marking the slow-moving eddies of the ocean surface waters. This false-color image shows the regions with high algae levels as bright red, orange, and yellow.* E. huxleyi *synthesize chlorophyll and carotenoids as well as alkenones that can be used as a measure of ocean temperature. Data like this can be transmitted to research vessels operating in the area to assist in sampling, or may be used to study large-scale phenomenon over long time periods.*

phytoplankton to depths where there is not enough light to carry out photosynthesis or sustain growth. Therefore, in winter the water column is characterized by a homogeneous distribution of pigments at low salt concentration. As winter storms subside and mixing lessens, algal growth and chlorophyll production begin to concentrate in the surface waters, the regions of highest light intensity, and a "spring bloom" is observed. Still later, as nutrients are depleted by the rapid algal growth that follows stratification of the water column, the pigment concentration decreases to "normal" open-ocean levels. The figure opposite illustrates this cycle of homogenization from deep mixing followed by water-column stratification, algal production, and finally a return to typical open-ocean conditions.

Measuring the carotenoid distribution in our samples reveals the dynamic changes in species composition that accompany the phytoplankton bloom. Our North Atlantic study focused on the distribution of three carotenoids that are characteristic of marine algae known to inhabit this area: peridinin from dinoflagellates, fucoxanthin from silica-forming diatoms, and 19'-hexanoyloxyfucoxanthin from carbonate-forming prymnesiophytes. In April, carotenoids, like chlorophylls, are homogeneously distributed throughout the water column. In our samples, peridinin, fucoxanthin, and hexanoyloxyfucoxanthin are present in approximately equal proportions, as are several other carotenoids characteristic of green and brown algae. This complex carotenoid distribution suggests that the turbulent but nutrient-rich conditions that characterize the water column in early spring can sustain many different algal classes.

Today, marine organic chemists often find unusual new compounds in sediments **before** *they have been identified in marine algae.*

With the onset of water-column stratification, phytoplankton begin to grow rapidly. Species better adapted to the new hydrographic conditions will out-compete other, less well-adapted species for nutrients, and eventually dominate the algal assemblage. This process is apparent in the pigment distribution of the June sample, which has a high fucoxanthin concentration from diatoms. As diatoms grow, they remove dissolved silica from seawater. Eventually, silica concentrations begin to decrease to levels where diatoms can no longer grow rapidly. At this point, other species of algae that do not require silica as a nutrient begin to dominate the pigments in our samples. The carotenoid distribution for the July sample shows that, indeed, diatoms represent only a fraction of the sampled phytoplankton. The dissolved silica concentration has decreased below the limit of detection, and pigments from prymnesiophyte algae begin to dominate our samples. By measuring the concentrations of these algal pigments with their characteristic structures, we were able to follow the complicated dynamics of biological species succession, which in turn affected seawater chemistry. This is just one way that organic compounds can be used as biomarkers to study environmental changes.

Molecular Thermometers: Reading Ocean Temperature from Algal Lipids

From the 1950s through the 1970s, organic geochemists analyzed sediments and seawater samples for compounds that had been previously identified in marine algae by natural products chemists (see Biomedical Uses for Natural Marine Chemicals, page 29). Today, marine organic chemists often find unusual new compounds in sediments *before* they have been identified in marine algae. In the late 1970s, organic geochemists at Delft University in The Netherlands found high concentrations of unusual lipids in Black Sea sediments. By using sophisticated spectrometric analysis they identified the unknown lipids as alkenones: long, linear molecules with 37 carbons. This discovery became important years later when organic geochemists working at Bristol University in England, along with marine biologists from the Marine Biological Laboratory in Plymouth, England, found alkenones in the coccolithophore *Emiliana huxleyi*, an important species of marine algae that has inhabited the world's oceans for 250,000 years.

Emiliana huxleyi makes a series of alkenones that differ in their numbers of double bonds, or sites of unsaturation. Alkenones with two or three double bonds are, in the jargon of organic geochemists, di- and triunsaturated compounds. Relative amounts of di- and triunsaturated alkenones in *E. huxleyi* change, according to the temperature of the ocean where algae live. We have long known that cells can regulate their membrane fluidity at different temperatures by changing the unsaturated-compound ratios of their membranes, but a direct correlation between temperature and organic compounds had never before been reported. This discovery raised the possibility that oceanographers could actually measure sea-surface temperature from alkenone distribution! If the temperature relationship was found to be robust, it offered geochemists a valuable tool to measure past changes in ocean temperature and climate from alkenones preserved in sediments.

The first test of alkenone paleothermometry was done at Bristol. A core deposited over the last 500,000 years (taken by the Ocean Drilling Program from the Kane Gap off northwest Africa) was analyzed for alkenones and oxygen-18, an established paleo-oceanographic tool for studying glacial-interglacial climate changes. A stable isotope of oxygen, oxygen-18 is a sensitive indicator of both temperature and the amount of water stored in polar ice caps. During glacial epochs, the average sea-surface temperature of northwest Africa was slightly lower than it was during interglacial times, and the amount of water stored at the poles was somewhat higher. These effects worked together to produce higher values for oxygen-18 in seawater, and ultimately, in the sedimentary record. The new alkenone-derived molecular thermometer shows similar swings in sea-surface temperature over the same glaciation-deglaciation transitions that oxygen-18 depicts. The alkenone record also reveals many previously unexpected, rapid temperature changes not identified in the isotopic record. We don't know the origin of these events, but they are probably related to major advances and retreats in the polar ice caps and other changes in ocean circulation.

The global climate has been subject to large temperature changes over glacial and interglacial cycles, but smaller climate disturbances occur over shorter time periods in the contemporary environment. Particularly interesting are the El Niño Southern Oscillation or ENSO events (see *Oceanus*, Summer 1984), climatic disturbances of variable intensity that last from several months to a year and occur once every two to ten years. El Niño most strongly affects the eastern tropical Pacific Ocean, but strong El Niños impact climate globally by influencing rainfall, wind pattern, and temperature distributions.

What causes El Niño, and how often do ENSO events occur? Organic geochemistry may be important to the study of ENSO phenomena, which are centered in the eastern tropical Pacific Ocean. During a "normal" year, the coastal ocean in this area is very cold and productive, due to wind-driven upwelling of cold, nutrient-rich waters along the Ecuadorian and Peruvian coasts. During an ENSO event, upwelling decreases, the water that is upwelled originates from a shallower depth, and is therefore warmer and nutrient depleted. ENSO events are characterized by coastal-ocean warming and a sharp coastal-productivity decrease.

We have attempted to reconstruct a history or geochronolgy of upwelling in the southeastern Pacific Ocean by studying the alkenone record of sea-surface temperatures in coastal sediments. We tested it by comparing a history of ENSO events over the past three centuries with alkenone-derived temperature

Technological innovations constantly change the way organic geochemists collect and analyze samples. Here technicians aboard the British R/V Discovery *deploy a new coring device that carefully collects undisturbed sediment samples from the seafloor. This "multi-coring" instrument allows geochemists to make high-resolution analyses on a suite of closely spaced samples. Other, similar advances have decreased the analysis time and materials by a thousandfold.*

data recovered from Peruvian sediments. There are a few caveats, however. First, while we have good measures of ENSO phenomena for this century (in the form of sea-surface temperature records), the El Niño records for the 17th and 18th centuries are indirectly derived from many sources, including temperature, annual rainfall, fish catches, and ship-transit time between Panama City and Peru. Together these historic records approximate a "best guess" of the situation. Second, to compare the historic and alkenone records, we must first know the sedimentation rate for our Peruvian core sample. We can measure this by using the naturally occurring radioisotope lead-210, but there are always errors and uncertainties involved, so the time scale and year-by-year record comparison may not be exact. Our comparison, however rough, shows that, indeed, the record of alkenone-derived ocean temperatures does seem to include the effect of ENSO events.

What Next?

The 1990s promise to be an exciting decade for organic geochemists. We know that several thousand organic compounds made by marine organisms respond to environmental changes in oxygen, pH, and temperature. We are just beginning to explore using molecular markers as both regional- and global-change indicators. Technology is providing us with new tools to sample previously inaccessible depths of the world's oceans, and to analyze the most complex mixtures of compounds found in sediments. For the first time, we have the capability to analyze the many thousands of samples required to study global phenomena. International oceanographic programs such as the Joint Global Ocean Flux Study will give organic geochemists around the world opportunities to cooperate and compare ideas and information as never before.

Technology is providing us with new tools to sample previously inaccessible depths of the world's oceans.

Like many marine chemists, Daniel J. Repeta developed his keen interest in oceanography while growing up in a landlocked state (Vermont). For the past 15 years he has puzzled over the chemistry of pigments and other organic constituents in algae and marine sediments. His current research is on the palaeoceanography of the Black Sea (a landlocked marine basin!) and the Peru upwelling area. He is an Associate Scientist in the Department of Marine Chemistry and Geochemistry at the Woods Hole Oceanographic Institution.

Cindy Lee became interested in oceanography while growing up in Arizona, which is even farther from the ocean and has even less water than Vermont. Her research interests include the chemistry of proteins and amino acids, and the impact of biological organisms on the distribution of nitrogenous compounds in the sea. Cindy is currently Professor of Marine Chemistry in the Institute of Marine Sciences at the State University of New York at Stony Brook.

Geoff Eglinton is Professor of Chemistry at Bristol University in England. His interests in organic geochemistry are wide-ranging, and have led him to work on six continents, numerous oceanographic cruises, and to the analysis of organic constituents of moon rocks, for which he was awarded a NASA Gold Medal for Exceptional Scientific Achievement. Geoff is a member of the Royal Society and a recipient of the Alfred E. Triebs Award for outstanding achievements in organic geochemistry.

Tracers in Oceanography

William J. Jenkins

Oceans carry heat and chemicals over great distances. As our activities impact Earth in more significant ways and we assume the mantle of stewardship for our planet, we must deepen our understanding of this important characteristic of the great organism we call our home. The urgency of this need is compounded because we are undoubtedly changing the way the oceans work, both directly by adding pollutants, and indirectly via climate modification caused by greenhouse-gas accumulation. Further, we *need* the oceans, as a purveyor of resources, transporter of ships, and source of food. Our quality of life and ultimately our future depend on how well we understand the oceans, not only in their present state, but also in the face of the profound changes we are making.

Much of our knowledge of ocean circulation, and indeed, the biological and chemical processes that are part of it, stems from studying distributions of the properties that determine water density, particularly heat and salinity (the amount of dissolved salts). Our general understanding of the grand, global thermohaline overturning (the sinking of cold, heavy water in polar regions, and their rise toward the surface in warmer climes) has also emerged from this work. The more subtle motions, such as chaotic and gradual interior flows coupled with mixing and turbulent diffusion, have been studied using tracers. "Tracers" are substances or properties of seawater that occur in such slight amounts (trace amounts) that they do not influence fluid motion. Indeed, some tracers have virtually no effect on normal chemical or biological processes, either. Tracers may be broadly categorized into three types:

- steady-state tracers, whose distributions do not vary in time,
- stationary-state tracers, whose distributions vary cyclically (seasonally, perhaps, or daily) in time, but whose average behavior does not change, and
- transient tracers, whose distributions are changing in time, usually due to humankind's influence.

In truth, there are very few steady-state tracers, and they are only moderately interesting because they can tell us little about how the oceans work. Some tracers, for example dissolved oxygen and inorganic nutrients, span the first two categories: They approximate a steady state in the deep ocean, but vary seasonally in the upper ocean. Observing the seasonal cycling of these tracers can provide us with quantitative infor-

"Tracers" are substances or properties of seawater that occur in such slight amounts that they do not influence fluid motion.

mation about biogeochemical and physical processes near the sea surface, but yield only qualitative information in deeper waters. Transient tracers are particularly interesting to oceanographers: Their distributions change with time, providing us with quantitative, and sometimes graphic information about physical and biogeochemical ocean processes. Some actual dating techniques have been developed that permit us to "date" water masses and trace their creation, evolution, and pathways through the ocean. Basically, the tracer geochemists' work is a mixture of careful sampling and analysis that is coupled with computer and mathematical models, then seasoned with a dash of imagination and intuition.

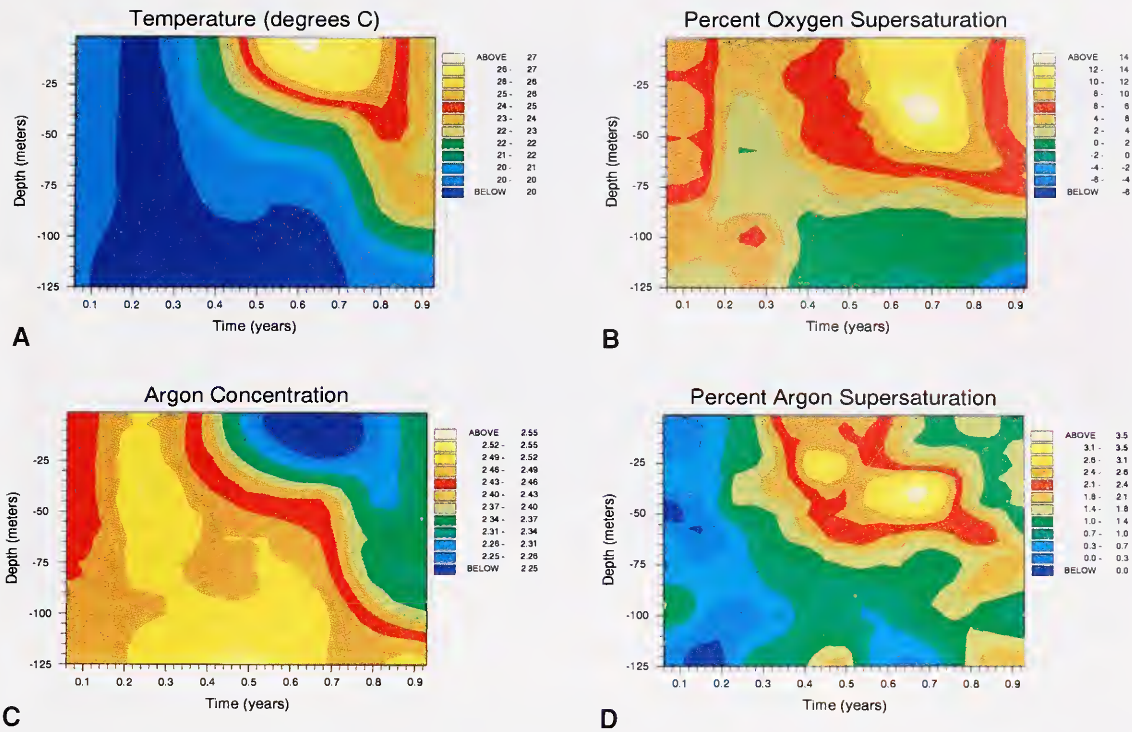
Steady- and Stationary-State Tracers

Steady- and stationary-state tracers have been studied the longest in oceanography, and have thus contributed the most to our knowledge of ocean circulation.

Transient tracer distributions change, providing quantitative, sometimes graphic, information about physical and biogeochemical ocean processes.

Shallow Oxygen. Dissolved oxygen is perhaps the most venerable of all tracers: It has been measured in seawater for many decades and is routinely recorded on almost every hydrographic expedition. Its principle cycle consists of photosynthetic production in the upper (euphotic) layer of the ocean, gas exchange with the atmosphere, and consumption in the deep sea by the bacterially mediated oxidation of organic material (see Photochemistry in the Oceans, page 36). Because the temperature, light cycle, wind stress, circulation, vertical mixing, and nutrient supply to the upper ocean vary seasonally, one expects (and indeed sees) a strong seasonal variation in biological activity, and hence dissolved-oxygen concentration. There is a remarkable annual cycle in the subtropics near Bermuda (see B, right). In early spring, after months of winter cooling, the water column is deeply mixed, usually to depths of 100 to 200 meters. Nutrients are mixed all the way to the surface, and winds force the water's dissolved gas concentration toward solubility equilibrium with the atmosphere. As spring sunshine begins to warm the water, the surface is "capped off" with a layer of warmer, lower-density water, and a seasonal thermocline (sharp temperature gradient) appears. This thermocline acts as a barrier to further vertical mixing, and oxygen produced by photosynthesis is trapped within it. A supersaturation in oxygen on the order of 15 percent develops by late summer, only to be destroyed along with the seasonal thermocline as autumn and winter mixing penetrates downward.

It should be possible to estimate the intensity of biological activity associated with this oxygen buildup, but how? Two problems arise. First, we know the thermocline is not a perfect barrier and some (perhaps most) of the biologically generated oxygen will be lost to the atmosphere. If we do not know the magnitude of vertical mixing, or the gas-exchange rate, how can we estimate this loss? Second, there are some physical processes that affect oxygen concentrations, the most significant of which is warming. Oxygen, like all gases, is more soluble in cold water. As water warms, oxygen will become supersaturated. This effect is visible when a glass of cold water is allowed to warm up: it becomes cloudy as gases come out of solution. Thus we have two competing processes: one that reduces the observed oxygen supersaturation, and one that increases



In the Sargasso Sea, warmer temperatures (A), are followed by increased oxygen saturation or supersaturation (B). Using argon as an oxygen tracer, scientists can account for the biology causing the oxygen supersaturation. Argon concentration (C) tracks the water temperature cycle, and argon supersaturation is three or four times smaller than oxygen supersaturation (D). The remaining oxygen supersaturation must correspond to biology.

it. Fortunately, nature has provided us with a key to unlock this mystery—argon.

The Noble Gases. The suite of noble gases on the periodic table of the elements presents us with a range of physical properties that we can use to "fingerprint" air-sea gas-exchange processes. Argon is in the middle of the noble gas column. Above it lies helium and neon, both being less soluble and more diffusive. Below it lies krypton and xenon, each being more soluble and less mobile. Noble gases are relatively stable, and are unaffected by chemical or biological ocean processes. Argon also has physical properties (solubility and molecular diffusivity, which is the rate that molecules diffuse through water) very similar to those of oxygen. For this reason we can use argon as an oxygen tracer, and account for those physical processes that affect oxygen's distribution. Knowing the physical processes, we can then deduce the biological rates.

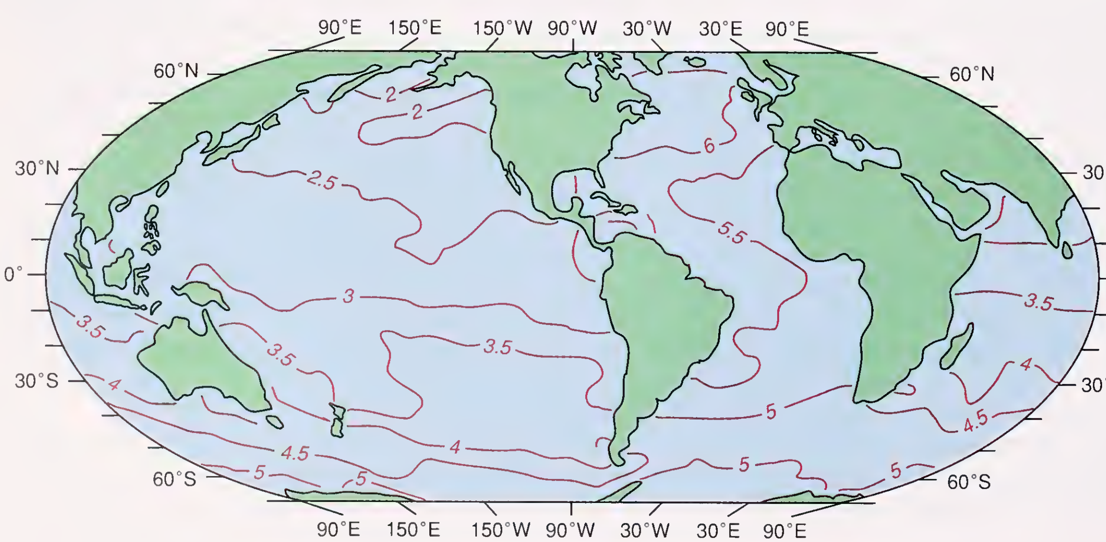
Here is how we do this. Above, C shows the argon distribution measured at the same site near Bermuda. Note how it tracks the temperature changes rather closely. What we are seeing is the upper ocean "breathing" argon in (in winter) and out (in summer), all due to argon's changing solubility with temperature. Remarkably, nature is kind to us, at least this time! As D shows, the ocean cannot breathe quite fast enough to keep up with the changing temperature, and residual supersaturation in argon remains, embedded within the thermocline. The argon maximum looks like the oxygen maximum, except that it is three to four times smaller, despite having nearly identical physical characteristics. We must conclude that the bulk of the oxygen maximum must be biological in origin.

The presence of argon supersaturation, its depth, magnitude, and timing, provide us with quantitative information about physical processes. Using an upper-ocean computer model and special mathematical methods called inverse techniques for comparing the model simulations with observations of temperature, argon, oxygen, and helium, we have made very accurate estimates of all the important physical and biological processes. By far the most interesting of these, however, is the computed rate of oxygen production. This estimate is about 6.2 moles of oxygen per square meter of ocean surface per year. Since about 1.7 moles of oxygen are produced for every mole of carbon "fixed" in photosynthesis, this leads to an estimated new production of about 3.7 moles of carbon per square meter per year. This rate greatly exceeded what was expected based on biological productivity measurements. Keep this number in mind; we will see a related estimate in the next section.

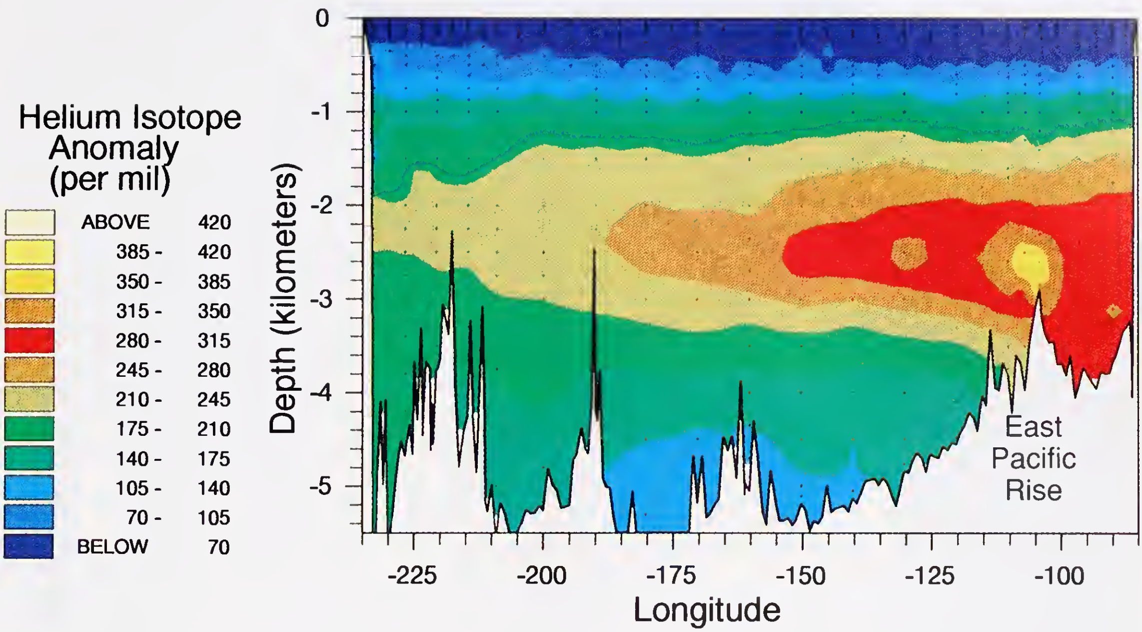
Gas cycling in the upper ocean is complex and interesting. It is relevant to our understanding of global biogeochemical cycling, yet many complicated processes occur at the air-water interface that are difficult to study. The technique we used to study the oxygen cycle may be extended if we study more of the noble gases. Armed with these potential surrogates, numerical models, and inverse techniques, we can learn more about these processes in a quantitative way.

Abyssal Signals. Throughout most of the abyssal ocean, dissolved oxygen is in steady state, meaning the oxygen supplied by the atmosphere from circulation and mixing exactly balances its removal by oxidation. Thus, if we were to visit and sample the same place now and again in a few months, years, or decades, we would find the same concentrations. Ocean circulation varies to some extent on all time scales, so this ideal is never completely realized, but for most purposes it is a useful approximation. In studying the distribution of dissolved oxygen in the world ocean at a depth of approximately 3,000 meters, we immediately identify the effects of global thermohaline circulation: Young, highly oxygenated water appears to sink in the polar North Atlantic, spread southward along the western boundary, travel around the Antarctic circumpolar regions, and invade the Indian and Pacific oceans.

The distribution of dissolved oxygen in the world ocean at approximately 3,000 meters offers a useful approximation of global thermohaline circulation. Young, highly oxygenated waters sink in the polar North Atlantic, spread southward along the western boundary, travel around the Antarctic circumpolar regions, and invade the Indian and Pacific oceans. Gradually, the dissolved oxygen reduces (as it is consumed). Minimal values exist in the northeastern Pacific.



Primordial Helium-3 in the Pacific



This helium-3 plume is situated just north of the equator, along 9.5°N (North America is on the right). The dominant feature in the helium-3 distribution is the large plume at middepth extending westward from the East Pacific Rise crest. Below it is the relatively helium-3–poor bottom water entering the North Pacific in the middle longitudes. Nearer the surface, helium-3 decreases as it is lost to the atmosphere. The plume's most remarkable character, however, is that it points in a direction opposite to that expected for deep-water flow.

As this water progresses, we see a gradual reduction in dissolved oxygen due to incessant consumption. This appears to culminate in minimal values in the northeastern cul-de-sac of the Pacific Ocean, where the world's oldest waters lie at great depths. From this we gain clear insight into global circulation, but things are not so simple!

Regions of intense oxygen deprivation are further up the water column, particularly in the eastern tropical Pacific and the northwestern Indian oceans. The Pacific minimum takes the form of two tongues of low-oxygen water extending westward at about 10° latitude north and south of the equator. A similar, fainter feature exists in the Atlantic. Do these features result from stagnation, where water ventilation (water's communication with or exposure to the atmosphere) is minimal, or are they due to zones of high biological activity in the waters above? The answer is most certainly the latter, and quite possibly the former. The eastern tropical zones of the Atlantic and Pacific oceans are characterized by wind-induced upwelling of nutrient-rich water that fuels tremendous biological productivity. The inescapable loss of particulate carbon downward from all this near-surface activity produces a strong oxygen demand, as is confirmed by sediment-trap results. However, these are also zones where circulation theories predict relatively poor ventilation, so the intensity of the oxygen minima may be linked to circulation features as well as biological activity. Which is more important? Are the two linked? If we can establish the ventilation rate, the rate of oxygen supply to the ocean interior at any point, we could deduce the net oxygen demand. This would help us resolve these kinds of questions. Ways to begin to do this are discussed under the transient-tracer heading.

Before we leave the steady-state tracers, however, there is another interesting tracer we can examine. Helium, the lightest of the noble gases, is the second most abundant element in the universe. Despite

this, it is rare in the atmosphere because it is lost to outer space. What helium we do have in the atmosphere and oceans results from the leakage of radiogenic and primordial helium from Earth's crust and mantle. This helium is comparatively rich in its lighter isotope, helium-3. Not only is this leakage of geological and geophysical importance, it also tells an interesting story about (and may even cause) some aspects of deep-ocean circulation. A noble gas, helium is unaffected by biological or chemical cycling, so its distribution is simple to interpret; in addition, since it is introduced into the ocean principally at mid-depths and in special (volcanically active) places, it has a unique distribution.

Like it or not, we have embarked on a grand geochemical experiment of global proportions.

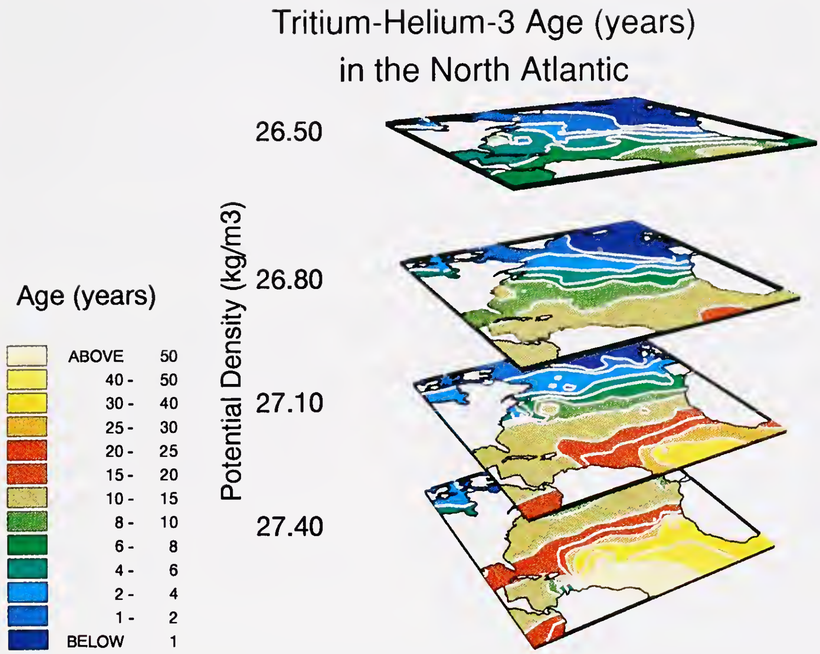
The imprint of this primordial helium-3 is most dramatic in the deep Pacific, in part because the water is oldest there, but largely because the rate of seafloor spreading and helium-3 injection is greatest in the Pacific. Here, one sees huge plumes of helium-3 spreading westward from the crest of the East Pacific Rise. Deep-water circulation theories predict a generally cyclonic (here eastward) flow, whereas this plume points westward. In a stroke of genius, the late Henry Stommel devised a theory in which the heat that accompanies this primordial helium-3 drives a deep flow that runs counter to global patterns. What we are seeing is volcanically driven circulation that extends thousands of kilometers across the ocean! Stommel's discovery was inspired by observing a helium-3 plume much like the one shown on page 51.

There are many other steady-state tracers, each with its own unique story to tell, and each with its own challenges, but we will proceed now to a different type of tracer, which has yet another approach—and other, additional challenges.

Transient Tracers

Transient tracers are challenging for two reasons. First, they are usually present in extremely minute quantities (largely because they are man-made), and are overshadowed by the vastness of the ocean through which they move. Measuring transient tracers often requires almost heroic efforts, with cutting-edge technology. The tracer geochemist also needs to pay careful attention to contamination problems that can, at times, prove daunting. Second, the manner in which these tracers enter the ocean is not well documented or controlled. Transient tracers are unwanted byproducts of industrial and military activities that are not always monitored or reported. Sometimes the tracer's origin is part of the mystery.

Humanity has, unfortunately, left a mark on the world. Unwanted byproducts of our personal, industrial, and military activities are entering the environment and causing serious problems: Witness the ozone hole now opening up in the northern hemisphere on the heels of that in the southern hemisphere, the greenhouse (global warming) effect, and land, groundwater, and coastal pollution. The silver linings in these environmental clouds, however, are the opportunities presented by the passage of these substances into and through the environment, and their impact on the systems they perturb. Like it or not, we have embarked on a grand geochemical experiment of global proportions. Perhaps by careful observation and thoughtful analysis we can learn enough about



These isopycnals outcrop or reach the ocean surface in the northeastern Atlantic, but dip downward in the subtropics, reaching their maximum depth in the "bowl" of the subtropical gyre, then shoal toward the equator. The 26.8 surface, for example, reaches a maximum depth of about 600 meters, whereas the 27.4 surface goes as deep as 1,000 meters. Because these surfaces comprise the bulk of the subtropical main thermocline, we are actually viewing thermocline ventilation.

the ocean-atmosphere system that we can prevent, or at least ameliorate, major environmental disasters.

Tritium-Helium Dating. In the two decades following World War II, nuclear weapons testing, principally in the northern hemisphere, introduced vast quantities of radioactive material into the environment. Concern about the effects of radioactive "fallout" led to a test ban in the mid-1960s, but traces of these substances persist in the oceans. One of the more useful of these is tritium, hydrogen's heaviest isotope. Chemically it is hydrogen, so tritium exists in the hydrosphere only as part of water molecules; thus is an ideal tracer for water movement. Tritium produced by nuclear weapons tests has totally overshadowed the "background" of naturally occurring tritium, similar to injecting a dye into the global hydrologic system. The spread of this tritium "dye" into the oceans has produced many striking pictures of ocean ventilation, further elucidating ocean-circulation rates and the magnitude of water-parcel mixing. To extract useful, quantitative information, however, requires careful modeling, developing a deeper understanding of the global hydrological system, and knowing the precise manner in which tritium has entered the ocean. We are making progress in these areas, especially in reconstructing the space-and-time histories of tritium concentrations in precipitation, atmospheric water-vapor transport, and isotopic exchange rates with the ocean. As our knowledge of these processes improves, so does our ability to use tritium to diagnose ocean circulation.

Another useful characteristic of tritium is that it is radioactive, decaying with a half-life of 12.45 years to the stable, inert isotope helium-3 that we discussed earlier. This provides us with a valuable tool. Consider a water parcel at the sea surface. This parcel has tritium, which

is constantly decaying, producing helium-3 that escapes to the atmosphere. If the water parcel leaves the ocean surface, this helium-3 can no longer escape, and so it accumulates at a rate controlled solely by the tritium concentration in the water. We thus have a "clock" that tells us how long it has been since a water parcel has been at the ocean surface. We can compute the "tritium–helium-3 age" from the measured tritium and helium-3 concentrations. With present measurement capabilities, we can detect times as short as two months, or as long as a few decades. These time scales are critical to understanding many environmental and climate issues.

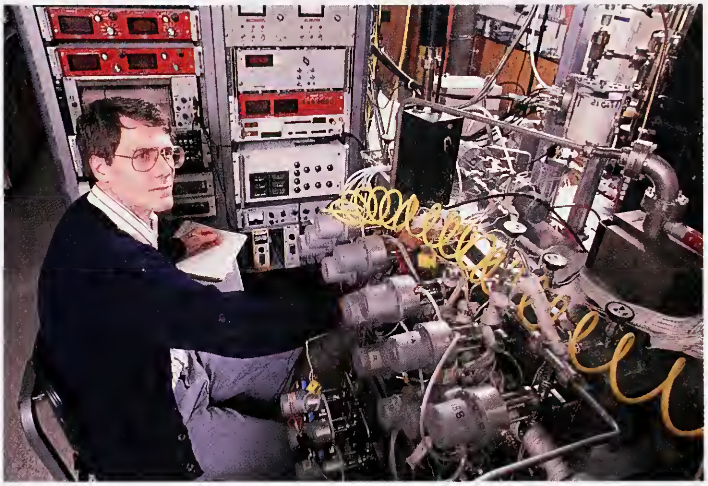
Helium-3 provides a "clock" that tells us how long it has been since a water parcel has been at the ocean surface.

As before, a few concerns about this simple approach warrant mention. There is an additional helium-3 source in the ocean, the primordial helium we discussed in the previous section. Fortunately, many parts of the ocean, particularly the shallow ocean, bear only a small, insignificant imprint of this type of helium. Primordial helium is most abundant in deep waters, particularly in the deep Pacific. Tritium, and "tritiugenic" helium-3 (produced by the decay of tritium) are found in shallow waters, away from this interference. Further, we can use other tracers to correct for the presence of primordial helium in parts of the ocean where this is a problem. There will always be places where we must tread with caution, but there are many areas, for example the shallow North Atlantic, that are accessible with this tool.

Another concern is that a fluid parcel in the ocean eventually loses its identity due to mixing. The effect of mixing on the tritium–helium-3 age is complicated, because the properties it is computed from are themselves mixed. Much analysis has been done on this problem, by examining both actual observations and computer-model simulations of ocean circulation. A good rule of thumb is that the tritium–helium-3 age is generally valid on time scales of less than a decade, but must be viewed with caution on times longer than 15 to 20 years. Even then, useful, qualitative information can be gained about the ventilation and spread of water masses, provided appropriate corrections and models are applied.

Using tritium–helium-3 dating, we can actually visualize ocean ventilation. In the figure on page 53, we see the tritium–helium-3 age distribution of four isopycnal surfaces (layers of constant density, along which water tends to move and mix) in the North Atlantic Ocean. Note that the age scale is not uniform, but emphasizes the younger ages. Also, the youngest water is north, where ventilation occurs by deep convection, subduction into the main thermocline, and mixing. Older waters appear to intrude from the south. The shallowest isopycnal is ventilated in the eastern subtropical Atlantic, but going to deeper isopycnals, the region of ventilation rotates first northward and then westward. The gyre circulation is clearly imprinted on the shallowest surfaces, as the isochrons (contours of constant tritium–helium-3 age) are pulled around the clockwise circulation of the western subtropics. A poorly ventilated pool of older water is at the center of the gyre, which must be ventilated indirectly by mixing. Going deeper, we see more zonally (east-west) aligned isochrons. At the deepest surfaces, an interesting counterflow sets up: relatively young waters flow southward along the western boundary, and older South Atlantic interior waters advect northward.

These large-scale plots are considerably lacking in detail, particularly information on smaller-scale circulation that is important to ocean ventilation. For example, a sharp tritium–helium-3 age front occurs due to the Azores Current, and secondary circulations and mixing may play a role in ventilation, in tandem with more geographically distributed subduction. (The Azores Current is a southeastern extension of the Gulf Stream that crosses the Mid-Atlantic Ridge at about 35°N and steers southwest of the Azores. It brings relatively young water into the eastern basin.) These processes are the focus of an intensive study called the Subduction Experiment that employs subsurface floats, surface drifters, current meter and meteorological moorings, towed CTDs (conductivity/temperature/depth sensors) and tritium–helium-3 dating. Combining these very different measurements with such inherently different time and space scales will be both challenging and rewarding. Supported by the Office of Naval Research, this study incorporates investigators from four major US oceanographic institutions, and should provide us with notable insights into ocean subduction and ventilation.



Tom Kleindinst

Author Bill Jenkins performs chemical analyses with a mass spectrometer.

Oxygen Consumption Rates and Biological Production. An important benefit of quantifying ocean ventilation and circulation rates is that it permits us to determine oxygen-utilization rates. Recall from our earlier discussion that as water ages, its dissolved-oxygen content decreases due to consumption by bacterial oxidation of organic carbon. Knowing the age of the water and the oxygen deficit, we can compute the oxygen-utilization rate. We can further gain some independence from "initial conditions"—such as Did the water leave the surface with equilibrium dissolved-oxygen concentrations? and Was the tritium–helium-3 clock properly zeroed?—by observing the gradients in both tritium–helium-3 age and oxygen deficit. Reassuringly, both approaches give similar results.

Although interesting for its own sake, we can go one step further and sum the oxygen consumption rate over the water column at a given place to find the net water-column oxygen demand. This in turn must be linked to the organic-carbon flux within the water column. If this flux is due to particulate carbon raining from above, it must have escaped from the euphotic zone, that is, it must be "new primary production." Integrating the curve results in a net oxygen demand and an estimated carbon production that is consistent, within uncertainties, with the estimate based on shallow photosynthetic oxygen cycling. The fact that both agree—despite rather different approaches—lends credence to the results. What is further notable is that the first results are characterized by seasonal to annual time scales, whereas the deep results represent a longer, annual- to decadal-time scale average. These time-scale issues are critical because biological processes, and the physical processes that influence them, must vary over time.

Final Thoughts

We have come full circle. Starting with observations of oxygen distributions, we began to build intuition about ocean circulation, but were plagued by ambiguity between ventilation and biological oxygen demands. Looking at shallow-ocean gas cycling, we managed to quantify rates of biological production at the sea surface, but the results were unexpectedly high. Turning to transient tracers, we are gaining quantitative knowledge of ocean ventilation rates, and in doing so, rates of oxygen consumption. These two lead us to the same kinds of numbers, reassuring us that we are on the right track. Most importantly, we are beginning to remove the shroud of ambiguity that cloaks the meaning of deep-oxygen distributions, and to better understand large-scale ocean circulation and ventilation. Each tracer has its own story to tell; as we develop the techniques to listen to those tales, we will gain a broader, deeper understanding of the oceans.

William J. Jenkins is a Senior Scientist in the Department of Marine Chemistry and Geochemistry at the Woods Hole Oceanographic Institution. He obtained his Ph.D. in nuclear physics at McMaster University in Canada, but somehow ended up in the Chemistry Department at Woods Hole. He is still trying to understand how this happened, and would be grateful for some kind of explanation. He has been interested in (and sometimes contributed to) the fields of solid-earth geochemistry and mantle structure, sediment pore-water transport, large-scale ocean circulation and ventilation, and biological productivity. He is particularly adept at annoying biological oceanographers with large space- and time-scale estimates of productivity. He has been fortunate to win the Rosenstiel Medal and the Clark Chair for Excellence in Oceanography, and to be elected a Fellow of the American Geophysical Union.

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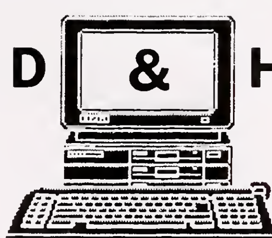

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US JOINT GLOBAL OCEAN FLUX STUDY PROGRAM

THE OCEAN'S ROLE in the global carbon cycle has attracted the interest of scientists from diverse disciplines for more than half a century, an interest sharpened in recent years by concerns about the effects of human activity upon atmospheric levels of carbon dioxide (CO_2) and other greenhouse gases. The Joint Global Ocean Flux Study (JGOFS) builds on accumulated knowledge about the ocean's chemical, biological, and physical processes to increase understanding of the ocean carbon cycle.

The program has two primary goals:

- to determine at a global level the processes that control the movement of carbon and other biologically active elements in the ocean and the way this cycling interacts with the atmosphere, the ocean margins, and the seafloor; and
- to improve our ability to make global-scale predictions of the likely response of ocean processes to changes in climate associated with human activities.

The US JGOFS program grew out of the recommendations of a 1984 National Academy of Sciences workshop. It is a major component of an international program, established three years later, which now numbers more than 30 nations among its participants.

Among the basic questions that underlie JGOFS research are the following: Which oceanic cycles are most susceptible to disturbance? How well do we understand these cycles, and how well do we need to understand them to achieve the goals of JGOFS? How detailed must our observations be in order to detect change? What new observing technologies can we apply to the problem of studying a living, moving, changing ocean?

The US JGOFS strategy for answering these questions has five major components:

- A global survey of oceanic properties and processes that will collect data needed for developing global-scale models and calibrating and validating satellite observations of ocean color (a measure of plant pigments in the sea);
- Time-series observations of long duration at key oceanic sites;
- A set of process studies designed to improve fundamental understanding of biogeochemical ocean processes and set parameters for modeling efforts;
- Development of models to assimilate results, produce global descriptions, and predict oceanic responses to future disturbances; and
- Development of an accessible, comprehensive biogeochemical database.

The US JGOFS program is under way in each of these five areas. As part of the global survey component, US JGOFS investigators are participating in World Ocean Circulation Experiment cruises and measuring carbon dioxide and ocean optics. Recently completed surveys in the Pacific have yielded data on variation in carbon dioxide levels at the sea surface. The bio-optical measurements will provide data for estimating the amount and distribution of phytoplankton in surface waters and correlating these results with satellite observations of ocean color. By late 1993, the US JGOFS program will begin to receive data from SeaWiFS (Sea viewing Wide Field Sensor), an instrument designed to measure ocean color

US JGOFS PLANNING OFFICE

from a satellite. This information, coupled with observations from ships and buoys on the ocean's surface, will enable investigators to begin to assemble a global-scale picture of phytoplankton stocks and to derive estimates of biological production in the ocean.

In 1988, the US JGOFS program established long-term, time-series stations near Bermuda and Hawaii. After three full years of monthly measurements, both programs have amassed substantial data sets and are beginning to report preliminary findings. Observers at both sites are noting surprising levels of variability in key processes such as primary production (photosynthetic conversion of carbon dioxide to live plant cells) and carbon fluxes, illustrating the need to develop methods for continuous monitoring to capture short-term variations over time.

JGOFS process studies began in 1989 with a pilot project in the North Atlantic. US investigators and research vessels *Atlantis II* and *Endeavor* participated in a five-nation study of the spring phytoplankton bloom that was designed to test plans for the full-scale process studies to follow. The first collection of papers from the project will be published this summer. Among the important contributions of this initial study are the refinement of techniques for measuring oceanic carbon dioxide and the collection of a large set of data on its seasonal and spatial distribution. The observations in the North Atlantic established that carbon dioxide variability in temperate ocean regions is strongly tied to the biological dynamics of the phytoplankton bloom.

The first full-scale US JGOFS process study is currently under way in the equatorial Pacific, where researchers are making a wide variety of measurements in a region regarded as a major source of atmospheric carbon dioxide. Process studies are also planned during the next few years for the Arabian Sea and the Southern Ocean. The monsoons of the Arabian Sea drive a uniquely intense carbon cycling system. The Southern Ocean may be a major sink for atmospheric carbon dioxide, and the large pool of unused nutrients in its surface waters offers great potential for changes in productivity. US JGOFS researchers are also assessing the feasibility of performing a small-scale process study in the open ocean to test the hypothesis that availability of iron limits the growth of phytoplankton in areas of the ocean rich in nutrients such as nitrogen and phosphorus. The objective would be to determine whether adding iron to these areas would increase oceanic phytoplankton production and thereby increase the flux of carbon dioxide from the atmosphere into the ocean.

Recent advances in modeling oceanic processes are assisting the process study currently underway in the equatorial Pacific. US JGOFS modelers have succeeded in linking a physical circulation model for the tropical Pacific with an ecosystem model to reproduce some of the most significant biogeochemical and physical characteristics of the region. US JGOFS data is accumulating steadily and will be readily available to all participants. This data set,

and the models developed through its use, will be the ultimate legacy of JGOFS.

US JGOFS is a component of the US Global Change Research Program. Although its funding comes primarily from the National Science Foundation, US JGOFS also receives support from the National Oceanic and Atmospheric Administration, the National Aeronautics and Space Administration, the Department of Energy, the Office of Naval Research, and the Environmental Protection Agency.

This article was synthesized by Hugh D. Livingston and Margaret C. Bowles of the US JGOFS Planning Office at Woods Hole Oceanographic Institution, from material provided by members of the US JGOFS Steering Committee.

Polly Williamson/IOS Deacon Laboratory

The platform deployment for the 1989 North Atlantic Bloom Experiment reveals the multinational approach JGOFS supports in answering long-standing questions about global ocean flux.

Particles in the Oceans

Jack Dymond

For most parts of the ocean, either living organisms or their products are the dominant particle forms.

On the whole, the oceans are remarkably clear bodies of water: One liter of open-ocean water typically contains less than 1/10,000th of a gram of solid particles. This means that particles comprise only one in 10 million parts of ocean water. One might think these small quantities of particles would play little, if any, role in ocean chemistry or overall ocean processes, but this view is far from true. The scant particle load and its movement through the ocean system influence seawater's chemical composition, and reflect major marine biological and geological processes.

The importance of particles follows from their continuous flow through the ocean system. The oceans are receptacles for products of continental erosion and weathering. Particles enter the oceans via rivers, the atmosphere, and as a result of shoreline erosion. On average, the particle-addition rate equals the removal rate as particles settle out of the water column: Because the oceans are not getting more cloudy with time, the particles entering must also be leaving. In part, mud accumulations on the seafloor reflect the input and settling out of these continentally derived particles through time. But in addition to these external particle sources, there are also particle-forming processes in the oceans. Activities of living organisms transform seawater's dissolved elements into a large array of particle types. In fact, for most parts of the ocean, either living organisms or their products are the dominant particle forms. Consequently, both the solid and dissolved inputs from continental weathering and erosion eventually end up as particulate material that settles through the water column and is buried on the ocean floor.

Particle Settling Processes

Most particles in the ocean are so small that we might expect them to take tens to hundreds of years to settle through the vast depths to the seafloor. If ocean particles settle so slowly, currents that flow at all depths should obliterate any geographic patterns of continental sources or biological distributions. A particle that enters the ocean might travel thousands of miles before coming to rest on the ocean floor; for example, clay particles carried into the ocean by the Saint Lawrence River might end up on the ocean floor off England, and an opaline shell from a tropical diatom species living along the equator might be found in

sediments off Greenland. Slow settling rates, therefore, pose a dilemma, since we know that ocean sediments offshore of rivers are similar to those carried by rivers. Also, fossil remains of organisms in marine sediments seem to reflect the type of organisms that inhabited overlying near-surface waters. If long-distance transport of slowly settling particles were the rule, there would be no relationship between the type of seafloor sediments and upper water-column processes, and it would be impossible to use ocean sediments as a record of biological processes or continental inputs into ancient oceans.

We can resolve this apparent dilemma because research shows that small, individual particles are quickly transformed into larger aggregates that settle much more rapidly. Large particles settle much faster and have far greater mass than small particles, so despite their scarcity they dominate ocean-particle removal. For example, the material removed from the oceans by 100,000 settling particles roughly equals the settling of a single particle that has a diameter 10 times larger. Recognizing this fact has led to the development of methods for studying specific classes of ocean particles. We must use different tools for studying slowly settling particles than we use for rapidly settling particles. Fine particles can be filtered out of the water, weighed, and analyzed. Alternatively, optical devices that measure water cloudiness can determine the abundance of fine particles. Large, rapidly settling particles are also captured through filtration, but their abundance is very low; therefore, most large-particle studies involve suspending devices called sediment traps in the water column to collect particles as they settle.

Funnel-shaped sediment traps are moored at various ocean depths for as long as two-years for studies of particulate flux in the water column. Individual samples cover about two weeks.

S. Honjo/WHOI

Just how are small, slowly settling particles transformed into relatively large, rapidly settling particles? Aggregation is generally thought to involve products of living and dead organisms. For example, many marine animals feed on phytoplankton and smaller animals. These animals (the zooplankton) release their waste products as rapidly sinking fecal pellets that often contain non-nutritious phytoplankton shells. Some zooplankton even indiscriminately gobble up continental erosion products, including inorganic mineral particles. In this way, fine mineral grains that otherwise would settle extremely slowly are incorporated into fecal material that travels rapidly to the bottom.

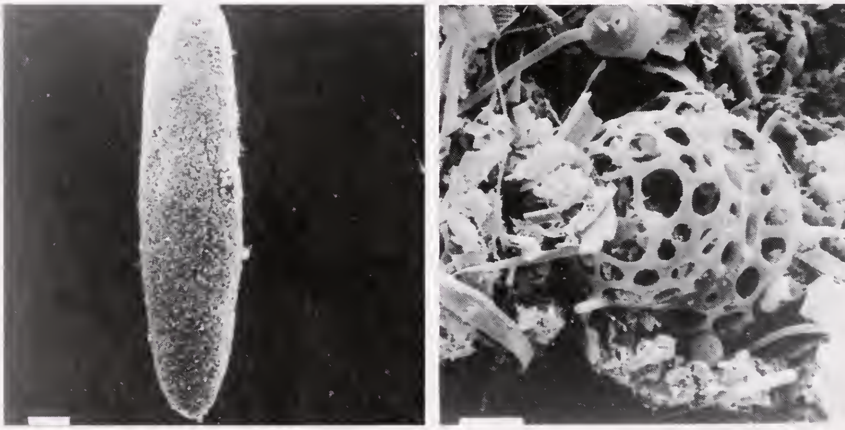
Other large aggregates known as marine snow form another means of transporting fine particles to the ocean floor. Marine snow looks like the more familiar atmospheric snow: Irregularly shaped particles clearly

visible to the human eye gently settle throughout the water column. These particles are loose aggregates of algae, decomposing bodies of small animals, bacteria, and fecal matter. As they fall through the water column, they may encounter fine mineral grains and incorporate them into the marine snow. In this way marine snow cleanses the ocean just as its terrestrial counterpart cleanses the atmosphere by removing smoke and other particles while settling to Earth. It is generally believed that settling of marine snow is the primary mechanism for removing particulate material from the oceans. Various studies have shown that these large-particle aggregates settle approximately 100 meters each day, in which case they would traverse typical ocean depths in roughly a month. This explains why radioactivity produced by the Chernobyl reactor explosion was found on particles more than 1,000 meters deep in the Black Sea within a month of the accident.

Because biological processes are primarily responsible for particle formation and removal in the oceans, it is not surprising that there is a relationship between productivity and the amount of particles settling. Nearly all photosynthetic organisms (the marine food chain's drivers) reside in the upper 200 meters of water. One might imagine that after a life of drifting in the clear, azure-blue ocean waters, these small organisms either die or are eaten, whereby they aggregate into particles that settle rapidly to the seafloor and become part of the sediment record.

The Importance of Recycling

Such a simple scenario, involving only life, death, and burial, however, is not quite how oceans work. Life on Earth has evolved in such a way that organisms' primary components, carbon and major nutrients, are efficiently recycled. As biologically formed particles settle through the oceans, they are constantly feasted upon by bacteria and other organisms. As a result, few particles found in the sunlit ocean settle directly into the deeper ocean. The elements and compounds that make up the tissue and shells of dead organisms are converted into the tissue of other organisms or, through bacterial decomposition, are transformed back into a dissolved form. In fact, it is probable that elements making up the tissue of small plankton will be returned to seawater as dissolved compounds to be used again by plankton many times before settling from the sunlit portion of the ocean. In this way, essential nutrients such

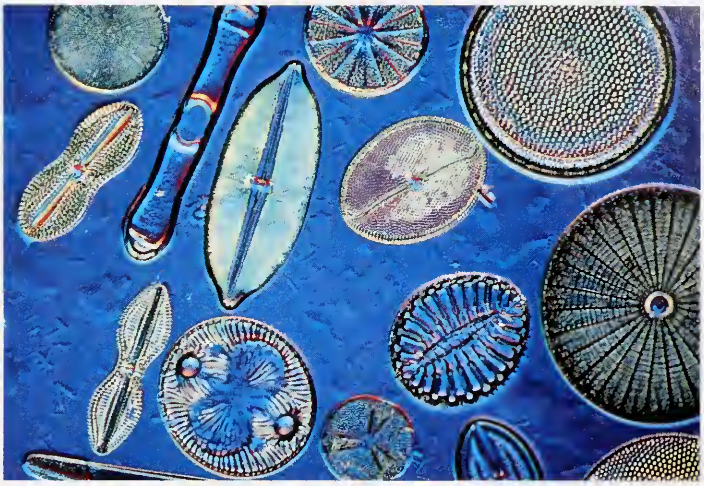


C. Pilskan/Monterey Bay Aquarium Research Institute

Marine snow and fecal pellets are the dominant settling-particle types in the ocean, and make the greatest contribution to carbon and nutrient flux from the upper to the deep ocean. The fecal pellet at right was trapped at the Clipperton Fracture Zone at a depth of 2,603 meters. The white bar at lower left shows a size reference of 50 micrometers.The radiolarian at far right, Lophophaena *sp., was found within the pellet. The size-reference bar for* Lophophaena *is 5 micrometers.*

as nitrogen and phosphorus become available to support even more photosynthetic activity.

Photosynthetic organisms living in the upper ocean also use nutrients that enter the ocean from the atmosphere and rivers. Even more important than these sources, however, are the nutrients carried by upward mixing of deep-ocean water. Deep-ocean water contains relatively high nutrient concentrations, and there is much more deep water mixed into surface water than is carried by rivers, making deep water a greater nutrient source than the atmosphere or rivers. Particle settling enters this story because the input of nutrients from atmospheric, river, and upward mixing sources must equal removal; otherwise, the oceans would soon lose their intense blue color and take on the green hues of an algae-choked pond. The settling of biologically formed particles is by far the dominant means of nutrient removal from the surface ocean. Even the remains of organisms that survive the scavengers and bacteria in the sunlit part of the ocean continue to be fed upon by other organisms as the remains settle into deep waters. As a result of the continuous toll on settling particles, less than 5 percent of the carbon taken up by phytoplankton in the upper ocean settles as particles to a depth of 500 meters, and roughly 1 percent makes it to the ocean floor. Although small and ever decreasing, the rain of particles through the water column is the only food for the diverse communities of organisms that scratch out a living at all ocean depths.



Jan Hinsch/Science Photo Library

"A cupful of water may contain millions upon millions of diatoms, tiny plant cells, each of them far too small to be seen by the human eye; or it may swarm with an infinitude of animal creatures, none larger than a dust mote, which live on plant cells still smaller than themselves."
—Rachel Carson,
The Sea Around Us

Life Without Recycling?

As a result of very efficient recycling schemes, far more life exists in the oceans than would otherwise be possible. Given the vast depths of the oceans, without recycling it is conceivable that any nutrients washed from the continents and removed from the upper waters as biological particles could be buried forever in dark, cold, inaccessible recesses. Such a system could support only a fraction of the life that currently exists. It is analogous to the level of technology that can be supported by a society that extracts critical metals and resources from rocks to make refrigerators and televisions and then buries them in landfills when the components wear out. The scale of technology in this case is limited by the rate at which resources are extracted from rocks. Should society choose to recycle the critical resources, the technological scale would be limited only by the efficiency of the recycling processes. Long ago the oceans evolved into a highly efficient recycling system that can support vast numbers of marine organisms.

Sediment Traps: Tools for Measuring Particle Flux

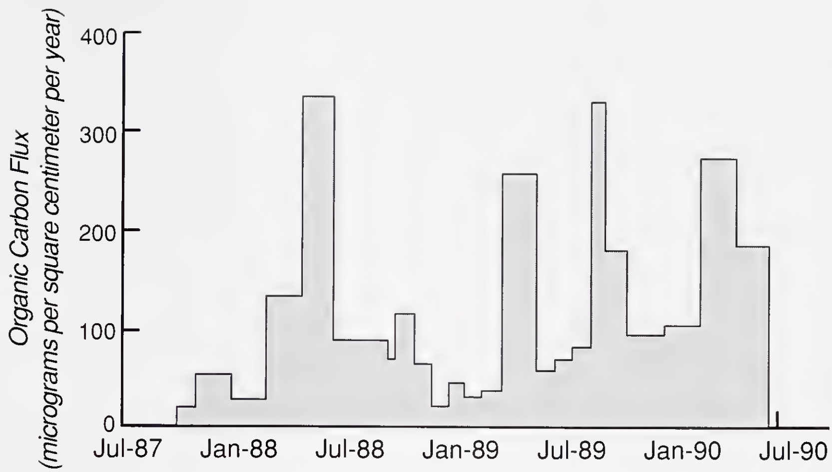
Much of our knowledge of particle settling comes from studies that collect particles at different depths in the ocean with sediment traps. A wide variety of trap designs have been developed. Most are cylinders or funnels that allow particles to enter through some sort of baffle at the top and then settle to the trap's bottom, where a bactericide inhibits sample decomposition. Recent designs also change sample cups electronically at preset intervals to collect sequential samples.

Questions regarding the accuracy of sediment trap results remain, but the available data make sense. The influence of trap design and ocean-current variations on particle-collecting efficiency has been and continues to be studied. For example, the flux of certain radioactive elements collected by moored traps is very similar to their production by radioactive decay of other elements, an agreement that suggests the trap collections are accurate. Elements carried by mineral particles of terrestrial origin that are not recycled in the oceans can also be used to evaluate sediment-trap accuracy. The particulate flux of these elements as estimated by sediment-trap studies is matched by element accumulations in sediment, reinforcing the sediment traps' apparent accuracy in recording particle-movement rates. One concern is organisms that swim into the traps and die, rather than settle passively as particles. New sediment-trap designs that exclude live, swimming organisms while still allowing passively settling particles to enter can address this problem. All things considered, we are confident that by using sediment traps we can define the processes controlling the transformation of dissolved carbon and nutrients into biological particles, as well as the timing of events that erode and carry continental materials to the oceans. An important feature of these instruments is that they are moored sensors that monitor ocean processes, allowing research ships and scientists to carry out other work. The traps are retrieved months or even years after deployment, with samples intact.

Chris Moser and Steve Manganini discuss the relative merits of sediment traps designed and built at their respective institutions (Oregon State University, left, and Woods Hole Oceanographic Institution, right). These traps were deployed in January 1992 as part of a joint OSU-WHOI study of particle fluxes across the equatorial Pacific Ocean.

Ocean Productivity, Particulate Carbon Flux, and Atmospheric Carbon Dioxide

Much has been written about global warming stemming from human-induced inputs of carbon dioxide and other greenhouse gases (see Balancing the Budget, page 18). Sediment-trap studies contribute to understanding this issue by helping to define the global carbon cycle, particularly the transfer of carbon from the upper ocean to deep-ocean waters. The uptake of carbon dioxide by marine plants (phytoplankton) during photosynthesis followed by the sinking of these biologically formed particles is commonly referred to as the "biological pump" or "tissue pump." This process lowers



These measurements of particulate organic carbon flux were taken in the North Pacific Ocean at 1,000 meters depth, over three years. Because organic carbon fluxes are controlled primarily by biological activity in the upper ocean, these measurements suggest a highly variable population of upper-ocean life. The highest carbon fluxes occur in late spring to early summer. Phytoplankton grow rapidly under the conditions of enhanced sunshine that occur in spring. Upward mixing by winter storms produces relatively abundant plant nutrients in near-surface waters, and solar heating leads to formation of a thermocline that confines phytoplankton to the sunlit zone. Such a scenario (followed by settling of biogenic particles) can explain the major features shown, as well as indicate that physical processes (wind and solar energy) control the timing of carbon and nutrient transfer via particles to the deep ocean.

the carbon dioxide content in the upper ocean and helps to transfer carbon to the deep ocean. The lower carbon dioxide content in near-surface waters enables more atmospheric carbon dioxide to enter the oceans by gas exchange processes than would be the case if the oceans were lifeless. As a result the atmospheric carbon dioxide concentration is maintained at a relatively low level. If photosynthetic activity in the sunlit portion of the ocean were to cease, the large amounts of dissolved carbon stored in the deep ocean would eventually equilibrate with the atmosphere and raise atmospheric carbon dioxide contents to levels nearly three times higher than those that exist today.

Sediment-trap studies coupled with other measurements in many parts of the oceans have led to estimates that 3 to 6 gigatons (a gigaton is a billion metric tones) of carbon are transferred each year to the deep ocean through the action of the biological pump. Although this is a sizable amount of carbon, the biological pump does not counterbalance the growing atmospheric carbon dioxide levels that are primarily a consequence of fossil-fuel burning. Despite increasing human inputs of carbon, the biological pump continues to operate at roughly the same rate, which only maintains the pre-industrial flows of carbon dioxide into and out of the ocean.

Some scientists have suggested that artificially increasing the oceans' fertility by adding the micronutrient iron to certain areas would increase the rate of biological pumping of carbon into the deep ocean. The effectiveness for carbon dioxide removal by this attempt at major ocean modification is still hotly debated, and its effects on upper and deep ocean ecosystems are currently unknown.

Particle Flux Variations

Just as different areas of the oceans support different amounts of biological activity, the flux of particles in the oceans varies greatly from place to place—probably by as much as 100 times. These variations reflect diversities in biological productivity of overlying waters and proximity to continental particle sources. The highest fluxes measured by sediment

traps are near the continents where coastal upwelling and rivers contribute nutrients and particles to the upper ocean. Although ocean margins cover a small area compared to the open ocean, high particle rain near the continents makes these areas surprisingly important as sinks for carbon, nutrients, and many dissolved elements that are found in seawater.

Sediment trap studies have also revealed that the amount of particulate material settling through the water column varies with different seasons and even between years. These variations reflect the ocean's dynamic nature. For example, the figure on page 65 shows that the rate at which organic carbon particles settle through North Pacific waters varies by about a factor of 10 over a three-year period. The variation seems to occur over a range of time scales that may be linked to atmospheric ocean dynamics. A seasonal pattern in the flux is the most prominent signal, but there are also particle-flux variations of both longer and shorter time scales than annual or seasonal. Short duration variations may reflect storms or other events that can mix nutrients from depth (for example the high flux in September 1989). Variability at time scales greater than one year may reflect either events like the southern Pacific's El Niño that modify the major wind systems and influence the extent of deep-ocean mixing, or they could indicate longer-term changes in climate such as those expected by global warming.

Particle-flux studies are providing new insights for interpreting the sediment record.

The Formation of Ocean Sediments from Particles

Over long time scales, elements carried by particles that make it through the gauntlet of bacteria and hungry organisms and are buried on the seafloor will approximately balance the elements introduced by continental and seafloor erosion. Hence, ocean sediments can be viewed as recorders of past weathering and climatic conditions. Because fluxes of particles to the seafloor reflect the biological productivity of the overlying waters, we might also expect to find a record of variations in productivity in the sediments. Has overall ocean productivity changed in the past? Have there been shifts in regions of high and low productivity that indicate changes in winds and ocean mixing? Have the amounts of carbon and nutrients buried in the oceans varied though time, and could these changes themselves affect the climate? Studies of the marine sedimentation record seek to answer questions such as these. Unfortunately, obtaining an accurate interpretation of sedimentation is not an easy task. Since much of the particulate material settling to the seafloor is recycled, the sediment record can be a biased or highly filtered representation of the original particle-forming processes, like the most filmy evidence at the scene of a crime. Only careful detective work can reveal the events that occurred.

Particle-flux studies are providing new insights for interpreting the sediment record. With sediment traps, the composition and flux of particles reaching the seafloor can be quantitatively defined. Comparing the particulate flux with that accumulating as sediments can reveal the amount of recycling of different components on the seafloor. In effect, this approach can be used to calibrate the sedimentary record. For example, carbon from plankton remains is the one sediment component that could be most directly related to upper-ocean productivity, but sediment-trap studies show that a variable fraction of raining particulate

carbon is buried and preserved in marine sediments. The amount of recycling seems to depend upon the total accumulation rate of the sediments: In areas with rapid sedimentation, perhaps near continents, or with high biological production levels, a greater fraction of carbon will be preserved. Such studies can help to transform the carbon-accumulation rate in sediments into a measure of ancient-ocean productivity, and overcome a long-standing problem in ocean-sediment studies, namely distinguishing productivity variations from changes in preservation.

Sediment-trap studies have also been used to calibrate other proxies for ocean productivity, the most promising of which is the element barium. Barium-rich particles (from the mineral barite) form in association with biological minerals, so barium flux in the oceans is strongly related to carbon flux and thus biological productivity. Barium is, however, much better preserved in sediments. Measurements of barium accumulation rates in sediments may be more accurate representations of ancient ocean biological productivity than carbon accumulation rates. Calibration of this and other productivity proxies using sediment traps make it possible to link upper-ocean biological processes with the seafloor processes that recycle and transform particulate material into preserved sediments.

Measurements of barium accumulation rates in sediments may be more accurate representations of ancient ocean biological productivity than carbon accumulation rates.

Because the ocean's biological productivity responds to climate and ocean circulation, the sediment record is a key for understanding ocean changes in different climatic regimes. This knowledge is critical if we are to fully understand the implications of global warming that is brought on by injecting greenhouse gases into the atmosphere. Over longer time periods (tens to hundreds of years) the interplay between climate, biological activity, and particle settling (which drives the carbon biological pump in the deep ocean) becomes complicated and unpredictable. Climatic changes may trigger variations in the oceanic ecosystem, causing particulate carbon and nutrient fluxes to change. Such fluctuations could lead to changes in atmospheric carbon dioxide content, which in turn would affect the climate. Some hypotheses hold that changes like this and the resulting feedbacks caused the glacial-interglacial climatic oscillations of Earth's past million years. They give us reason to reflect on the era of human-induced global warming that we are entering. At present, our knowledge of the interactions between climate and biological activity, particle formation, and sedimentation is inadequate to predict the outcome of this major change in the planetary ecosystem. We may find some surprises ahead.

Jack Dymond is Professor of Oceanography at Oregon State University. His research has ranged from pondering noble gas systematics of deep-ocean basalts to reflecting on the meaning of strange bacteria in the depths of Crater Lake. He was part of the original team that used DSV Alvin *to discover thermal springs and exotic vent fauna on the Galapagos Spreading Center in 1977. More recently he used the submersible to sample black smokers and even study the origin of ferromanganese nodules. He was the first person to go to the bottom of Crater Lake in a one-person submersible, where he discovered some very surprising saline pools of hydrothermal origin. He is currently involved in particle flux studies in the ocean and large lakes of the world in order to understand the relationship between sediment formation, biological processes, and atmosphere-ocean dynamics.*

Biogeochemical Processes on the Seafloor

Fred L. Sayles

Material released to solution through remineralization is recycled back into the ocean, to mix through it for roughly 500 to 1,000 years.

The deep-ocean seafloor is an integral part of the ocean-atmosphere system. Processes occurring at and near the sediment-water interface can strongly influence chemical concentrations in the surface ocean (especially nutrients essential to primary production), the composition of the atmosphere (particularly its carbon dioxide content), and the record of past climate that is preserved in the sediments themselves. The importance of seafloor processes to our understanding of the ocean and the way chemicals cycle through it, past and present, has fostered many studies of this region, accounting for some 70 percent of the solid earth's surface. These investigations have detailed the origin, nature, and rate of material delivery to many areas of the seafloor. In addition, we have learned much about the reactions occurring on the seafloor and the profound influence they have on the fate of all materials delivered to this critical interface.

Material delivered to the seafloor derives largely from two sources. The first is rivers, which supply the oceans with large quantities of debris created by continental land-mass weathering and terrestrial organic material from vegetation and soils. Much of this material is deposited on the continental margins, comprising a large part of the sediments of continental rises and slopes. The finer material delivered by rivers can be spread more broadly, finally settling to the seafloor thousands of kilometers from its source. The second major source of sedimenting material is the biological fallout from the upper 100 meters or so of the water column that sunlight penetrates. This material consists primarily of the skeletal remains of small organisms, largely calcium carbonate and silica, and organic matter. The organic matter is recycled efficiently in the upper 100 to 500 meters and only 1 to 10 percent of it escapes these shallow waters of the ocean. The bulk of the calcium carbonate, a significant fraction of the silica, and this small part of the organic matter are transferred to the seafloor relatively rapidly, on a time scale of months, with little further reaction. The rapid transfer of material between the surface ocean and the seafloor dictates that seafloor processes respond very rapidly to surface ocean conditions and,

particularly, changes in surface conditions that affect the production of particulate matter. It is this rapid response that makes the seafloor an integral component of the ocean-atmosphere system. A third source of material deserves mention, for it is responsible for the delivery of continental detritus at great distance from land masses. Wind-borne dust is broadly distributed over certain areas of the globe, and is an important source of continental detritus in regions remote from riverine sources. However, for 80 to 90 percent of the deep seafloor, the input of biogenic detritus strongly exceeds continental material.

The solids arriving at the seafloor suffer one of two fates: they are either "remineralized" (dissolved through various reactions) or buried in the accumulating sediments. The partitioning between remineralization and burial has a tremendous impact on the cycling of the elements involved, and through this, the chemistry of the oceans. Material released to solution through remineralization is recycled back into the ocean, to mix through it for roughly 500 to 1,000 years (the time scale of ocean mixing). These elements remain an active part of the system. The buried material enters a totally different cycle. Very ancient sediments are rare because sediments are recycled; however, the time scale of sedimentary recycling is measured in hundreds of millions of years. Buried material is thus effectively sequestered from the ocean-atmosphere system with its far faster cycle times. In a temporal sense, the seafloor is, indeed, one of the great "divides" of our planet. Fractionation at few other interfaces has such a tremendous effect on the time scales of sequestration.

In a temporal sense, the seafloor is one of the great "divides" of our planet.

The processes that determine the fractionation between remineralization and burial are interesting for a variety of reasons. Clearly these processes have a major impact upon element cycles. Changes in the proportion of burial versus recycling, especially for biologically active elements, can influence both ocean and atmosphere chemistry. The burial of material on the seafloor produces the most extensive record available to us of Earth's past. We use it not only to understand the evolution of Earth and its oceans, but also as a basis for predicting the future. This record contains the products of the surface ocean, but they have been modified greatly by the processes that lead to remineralization. The record contains only a residue, analogous in many ways to the ashes of previous civilizations that are so important to archaeological investigations. A knowledge of these modifications to the original inputs is a prerequisite to accurately deciphering the past record and predicting the future.

Studying Reactions on the Seafloor

Knowledge of seafloor sediment reactions comes primarily from studies of pore waters, the solutions that fill the spaces between solid grains of sediment. Although it may appear solid, deep-sea sediment is often 80 to 90 percent water. As reactions occur between solids and pore solutions, the solution composition changes, providing a sensitive indicator of the course of reactions. By using models of reaction and diffusion (the primary means of mass transport in sediments) as well as concentration measurements from various depths in the sediment, we can define the types of reactions and reaction rates, and identify exchanges between the

James E. Broda

sediment and overlying seawater, that is, the recycling of the solids delivered to the seafloor.

As with so many oceanographic studies, pore-water investigations seem to have originated with the *Challenger* Expedition; a report by J. Murray and R. Irvine, describing their efforts to extract and analyze waters from sediments, was published in 1895. Methods for studying pore waters have evolved considerably since then. For decades, cores of seafloor sediment have been collected and the pore waters extracted with specially designed "squeezers," developed in part by Russian scientist O.V. Shishkina and Frank Manheim (United States Geological Survey) in Woods Hole. In the early 1970s Paul Mangelsdorf, Jr. (working at Woods Hole Oceanographic Institution) and others discovered that temperature and pressure changes during core recovery were causing serious artifacts in the observed concentrations of many components, as a result of interactions between the solids and pore fluids. This led to development, largely in our lab, of in-situ (on the seafloor) pore-fluid extraction techniques that avoid these artifacts. Most advances carry associated costs, and in this case they were substantially increased size and complexity. The photos at left show a gravity core, the sampling tool used to collect many sediment cores, and the sampler developed in our lab to collect in-situ pore waters. With complexity often comes the potential for problems; the photo opposite illustrates a classic problem that resulted from trying to lower a large instrument package to the seafloor and leave it there undisturbed (on a slack wire) for 30 to 40 minutes while still attached to the ship some 3 to 4 miles above. Recent developments have increased complexity and sophistication yet another notch with the addition of "free-vehicles." These computer-controlled instruments are released, untethered, from their mother ships. They sink to the seafloor, complete preprogrammed measurements and/or experiments, then return to the surface with their acquired data. Free vehicles include "micro-profilers" that measure concentrations in situ on depth scales of millimeters and benthic landers capable of sampling, measurement, and experimentation (see Oceanographer's Tool Box on page 8).

A gravity corer (above) is landed on the deck of R/V Oceanus. *The corer is lowered into the seafloor to retrieve sediment cores 1 to 1.5 meters in length. Disturbing the uppermost layers of sediment is not uncommon with this approach, but the simplicity of the device makes it otherwise very reliable. The in situ sampler dubbed the WHIMP (Woods Hole Interstitial Marine Probe), shown at right with one of its operating teams, is far larger than the gravity corer. This instrument is able to reliably sample the sediment-water interface and to collect pore waters in situ.*

Reactions occur throughout the sediment column (to thousands of meters below the seafloor), but rates are greatest in the first meter below the seafloor: In general, about 85 percent of dissolved-element transfer between sediments and the ocean originates in the upper meter, and frequently in an even narrower interval. The importance of this interval in remineralization reactions and recycling of sedimenting material has led to a focus on it, especially the uppermost 1 to 10 centimeters. Work-

ing in this narrow interval from a ship 3 to 5 kilometers above the sample site without disturbing the sediment is no mean feat, and is a primary motivation for developing free vehicles.

Remineralization Reactions

While many different reactions occur in the sediments near the seafloor, almost all are associated, directly or indirectly, with biological activity. The most important reactions, in terms of mass transfer between the sediments and the oceans, are driven by the metabolic processes of deep-sea organisms. In the deep sea, food is extremely limited and is supplied by the organic component of settling particulate matter. Thus even in the dark abyss, most life ultimately depends on sunlight for its energy.

Deep-sea sediment metabolic reactions are most simply thought of as a sequence of chemical reactions that result in the oxidation of organic carbon to carbon dioxide and yield energy to the organism. The reactions occur, by and large, in a sequence determined by the energy yield of the reaction: the oxidant producing the largest energy yield is consumed first, then that producing the second largest yield, and so forth through the available oxidants. Unquestionably, specific organic compounds maximize energy gain with specific oxidants. However, our knowledge of the details of the composition of sedimentary organic matter and its oxidation remains rudimentary; the reacting material is usually treated as a single set of chemical components rather than as specific organic compounds. This approach has been sufficient to elucidate the general suite of oxidative reactions, but, undoubtedly, some surprises await us as we learn more of the details of the complex mixture that comprises sedimentary organic matter.

The primary oxidant in the oxidation sequence is oxygen, whose energy yield for a wide variety of compounds is greater by a wide margin than that for any other available oxidant. Because oxygen is abundant (200 to 300 micromoles per liter) in the bottom waters of all of the deep sea save restricted basins, it is by far the most important oxidant. Overall, oxygen oxidation consumes 70 to 80 percent of the organic matter oxidized in the upper meter of marine sediments; in most of the deep sea the proportion is closer to 95 percent. The second oxidant in the sequence, nitrate, is itself a product of the preceding oxygen reaction. Nitrate is also the second most important oxidant in open-ocean sediments in terms of the organic mass consumed, occasionally as much as one-third of the total. Together oxygen and nitrate account for about 90 percent of organic matter remineralized in the upper meter of deep-sea sediments and are thus by far the most important in recycling organic matter back into the ocean. The remaining oxidants, which can have important effects on the organic-matter content of sediments but much less on exchange with the ocean, include manganese dioxide, iron oxides, and sulfate. Manganese dioxide and iron oxide are delivered to the sediment primarily

This is one of the unpleasant surprises that occasionally greets researchers when recovering the WHIMP. Hanging from this snarl is a very expensive 2,000-pound instrument. The snarl contains about 50 meters of half-inch cable and is virtually impossible to unravel. As a consequence, the cable must be cut, an operation risky for both instrument and personnel—and the source of many of the author's prematurely gray hairs. This photo was taken aboard R/V New Horizon, *in the, fortunately, calm central Pacific.*

as particulate matter, while sulfate is a major anion (negatively charged component) of seawater. Manganese dioxide has an energy yield close to that of nitrate and their utilization can overlap. Iron oxide follows manganese dioxide, while sulfate is the least favored energetically and occurs only at considerable depth in most deep-sea sediments.

This sequence occurs in virtually all marine sediments, with only the depth scale of the onset of the different reactions varying. In deep sediments underlying poorly productive open-ocean surface waters, the sulfate zone may only be reached at depths of tens or hundreds of meters, or not at all. In shallow, productive coastal environments the high input of organic matter can lead to occurrence of the entire sequence in the upper few tens of centimeters. The net result of these reactions, and a reflection of the efficiency with which organic matter is utilized, is the consumption of about 90 percent of the organic matter delivered to the sediment-water interface in almost all environments and some 98 percent in most of the deep ocean.

Metabolism also produces side reactions that have a significant impact on remineralization of settling particulate matter as well as on sediment composition. One of the most important of these is the dissolution of calcium carbonate, the predominant skeletal material in the oceans and the single most abundant component of marine sediments. To understand this process, we must first look at the details of the various oxidation reactions discussed above. In particular, oxygen oxidation is differentiated from the other reactions by the production of carbonic acid (essentially, carbon dioxide) while the other reactions produce bicarbonate. The two most important reactions are shown below; reactants are on the left and products on the right. As a result of this difference, oxygen oxidation dissolves calcium carbonate in the sediments and the other three dissolve little or none, and can even cause calcium carbonate to precipitate.

Metabolism also produces side reactions that have a significant impact on remineralization of settling particulate matter as well as on sediment composition.

Pore waters, in a way, record reaction results. This can be seen quite easily just from inspecting pore-water depth versus concentration profiles. Solid organic matter reacts with oxygen from the pore waters

The Two Most Important Oxidant Reactions

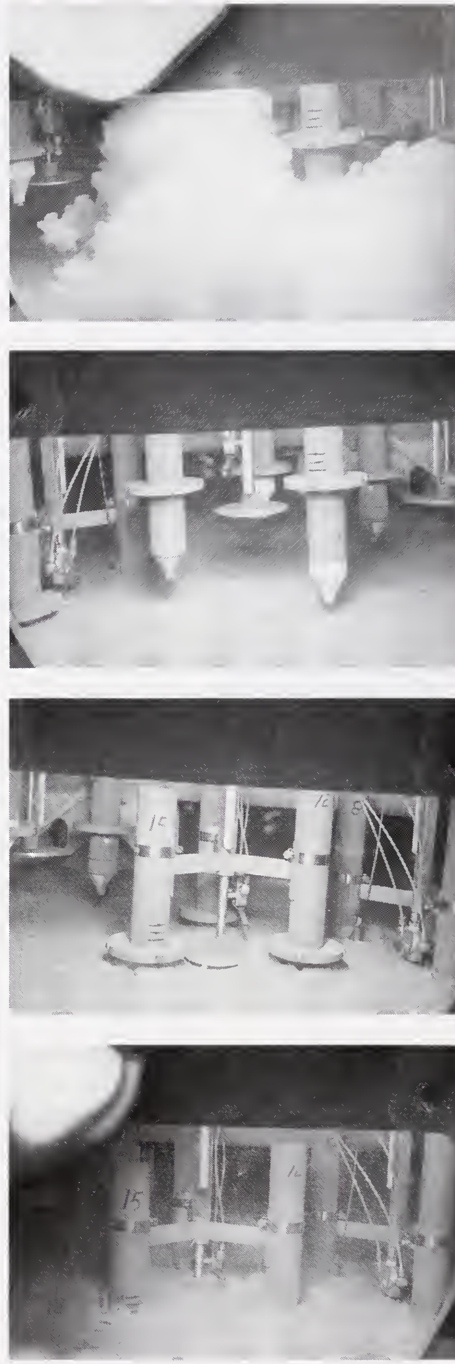
$$\underset{\text{organic matter}}{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)} + \underset{\text{oxygen}}{138\ O_2} + \underset{\text{calcium carbonate}}{124\ CaCO_3} \rightarrow \underset{\text{bicarbonate}}{106\ HCO_3^-} + \underset{\text{nitrate}}{16\ NO_3^-} + \underset{\text{phosphate}}{HPO_4^{2-}} + \underset{\text{calcium}}{124\ Ca^{2+}} + \underset{\text{water}}{16\ H_2O}$$

$$\underset{\text{organic matter}}{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)} + \underset{\text{nitrate}}{94.4\ NO_3^-} + \underset{\text{calcium carbonate}}{13.6\ CaCO_3} \rightarrow \underset{\text{bicarbonate}}{119.6\ HCO_3^-} + \underset{\text{nitrogen}}{55.2\ N_2} + \underset{\text{phosphate}}{HPO_4^{2-}} + \underset{\text{calcium}}{13.6\ Ca^{2+}} + \underset{\text{water}}{17.2\ H_2O}$$

The first term of each reaction is a schematic representation of the elemental composition of organic matter. For oxygen oxidation (the top equation), one "mole" of plankton consumes 138 moles of oxygen and dissolves 124 moles of calcium carbonate. Nitrate oxidation, however (the bottom equation), results in only about one-tenth as much calcium carbonate dissolution; 13.6 versus 124 moles. The other oxidant reactions (manganese dioxide, iron oxides, sulfate) are still more basic than nitrate and result in precipitation, rather than dissolution, of calcium carbonate. Thus from the view of calcium carbonate burial and recycling, the amount of organic matter being oxidized with oxygen, as opposed to others, is a critical factor.

and releases a number of components, among them nitrate. We would expect to see a loss of oxygen and concomitant gain of nitrate in the pore waters, and this is demonstrated quite clearly, as the oxygen concentration drops rapidly near the interface, reaching values of only about 25 percent of bottom water by about 1.5 centimeters. Had we extended our measurements another 1 or 2 centimeters we would have seen the oxygen disappear entirely. The nitrate concentrations increase, reaching a maximum at a depth of 1.5 centimeters. The sharp decrease in nitrate below 1.5 centimeters is caused by the exhaustion of oxygen at about 2.5 centimeters and the onset of nitrate oxidation; nitrate is consumed, reaching zero at a depth of about 7 centimeters. The other oxidants are also used in the sequence described above but, for the sake of simplicity, the components that record them are not included in the figure.

Under certain circumstances, calcium carbonate can dissolve in the ocean without the aid of acid from oxygen oxidation. This process can drastically affect the composition of the sediments and calcium carbonate burial. As with all materials, calcite, the common form of calcium carbonate in the ocean and sediments, will not dissolve in waters that are saturated or supersaturated; it will dissolve spontaneously when exposed to undersaturated waters. (Saturation is an expression of a mineral's tendency to dissolve into or precipitate out of its medium, which is seawater in this case. At saturation a mineral is at equilibrium and neither dissolves nor precipitates; at undersaturation it dissolves; at oversaturation it precipitates.) The saturation state of calcite varies substantially with depth in each of the earth's oceans: it is supersaturated in the upper ocean and passes to undersaturation at depths between 3,000 and 5,000 meters, depending on location. At depths somewhat below the boundary between supersaturation and undersaturation, the calcium carbonate of sediments is effectively dissolved simply by exposure to overlying (undersaturated) seawater. Above this horizon, dissolution requires the addition of an acid to the pore waters, the only significant source of which is the oxidation of organic matter described



The photo series above was taken by the WHIMP while landing on the seafloor. In the first picture, a cloud of sediment is resuspended by the WHIMP's feet as it lands. Within minutes currents have swept the material away and we can see the probes of the WHIMP being inserted in the sediment (second). The cones in the pictures are sampling elements; the white portions of the cones are filters through which pore solutions are drawn to separate them from the sediment. Each cone is fixed at a set distance below a sediment sensor; they are driven into the sediment until the sediment interface is sensed (third). Sampling then commences, yielding a set of 15 samples from preset depths in the sediment. These pictures were taken at 4,400 meters off the coast of Nova Scotia.

Were it not for benthic metabolism, the small but important fraction of total primary production that reaches the deep seafloor would be lost for hundreds of millions of years.

above. Thus even in the absence of any benthic metabolism, at depths below the saturation horizon, calcium carbonate can be effectively stripped from the sediments by a purely inorganic process.

The case of biogenic (formed by organisms) silica, the second most common skeletal component, is directly analogous to that of calcite with one important difference: The oceans are everywhere undersaturated with biogenic silica. As a consequence, it is subject to extensive dissolution in all sediments and is preserved in abundance only where the input from the surface ocean is so rapid that it overwhelms the rate of dissolution, most notably in the Antarctic Ocean where there is very little input of other sedimentary components. Its propensity for preservation versus dissolution is not affected by metabolic reactions.

Oxidation and dissolution can have a large impact on the nature of materials preserved in the sedimentary record. As noted above, 90 to 98 percent of the organic matter reaching the seafloor is metabolized. These reactions are essential to releasing the nutrient elements nitrogen and phosphorous back into the ocean system. Were it not for benthic metabolism, the small but important fraction of total primary production that reaches the deep seafloor would be lost for hundreds of millions of years; over time, this would have a drastic effect on the fertility of the oceans. To a lesser extent but in an analogous fashion, the calcium carbonate cycle would be altered. Dissolution driven by oxygen oxidation has been shown to remineralize some 30 to 50 percent of the calcium carbonate delivered to the seafloor above the saturation horizon. In the absence of metabolic dissolution, all of this material would be buried and removed from the ocean, sequestering substantial amounts of carbon dioxide. Thus seafloor reactions are an important and integral part of maintaining the ocean and atmosphere as we know them.

Reactions on the seafloor also impact our interpretations of the sedimentary record in terms of conditions prevailing in past oceans. The remains of calcareous organisms in sediments constitute our main information source on ocean conditions and processes for the past several hundred million years. Analyses of these remains provide data on temperature distributions, circulation patterns, seasonal variation in surface waters, and productivity. The dissolution of calcium carbonate attendant upon organic-matter oxidation modifies the material delivered from the surface, and must be taken into account in many aspects of paleo-ocean conditions. For example, changes in the rate that calcium carbonate accumulates in sediments has frequently been related to changes in the productivity of the overlying surface waters, faster accumulation being taken to be higher productivity. However, since a substantial fraction of the calcium carbonate input is dissolved within the sediments after delivery, the relationship of accumulation to surface productivity is not straightforward. In particular, since in situ dissolution is dependent upon two critical factors, the amount of oxidation occurring (organic carbon delivery) and the proportion of oxygen oxidation, accurate interpretation of the record must take these factors into account. In-situ dissolution can also affect our ability to reconstruct past current patterns. In some areas the boundary between saturation and undersaturation in the oceans is associated with the boundary between different water masses. Variation in the depth of rapid calcium

carbonate dissolution associated with the passage to undersaturated waters has been interpreted as being due to changes in water-mass circulation. These changes in calcium carbonate may also be due, in part at least, to variations in the conditions of organic-matter oxidation. In short, because benthic reactions significantly modify the character and proportions of material incorporated into the sedimentary record, interpreting this record must include a thorough understanding of these reactions, their impact on the sediments, and the signatures of their occurrence.

Where to Now?

We have learned the basics of reactions occurring on the seafloor and have a fair knowledge of the mass transfer between ocean and sediment that is driven by them. We know that the reactions taking place are linked quite closely to conditions in the surface ocean despite the spatial separation, and that the proportion of carbon oxidation by oxygen versus the other oxidants has a critical influence on sediment composition and calcium carbonate sequestration. This proportionality is linked to a number of factors that include the carbon delivery rate (itself a reflection of surface-water productivity) and the relative amounts of calcium carbonate and organic carbon delivered to the sediment, determined in part by distributions of calcareous and siliceous organisms in the surface waters. The next decade will focus on identifying the factors that control the relative importance of the various oxidation reactions and that also control preservation versus remineralization. We will continue to try to quantify the links between conditions in the surface ocean and reactions in the seafloor as they are not only critical keys to understanding the relative importance of the different reactions but are also essential to being able to read the record of the past surface ocean that is preserved in the sediment.

The next decade will focus on identifying the factors that control the relative importance of the various oxidation reactions and that also control preservation versus remineralization.

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Hydrothermal Activity in the Deep Sea

Intractable Problems and Lots of Questions

John M. Edmond and Karen L. Von Damm

Hot springs on the deep seafloor were first discovered in 1977 on the Galapagos Spreading Center, appropriately enough, northeast of the famous Galapagos Islands. Early formulations of the plate tectonic theory of seafloor spreading identified the mid-ocean ridges as Earth's most important loci of volcanism. This immediately prompted the suggestion that pervasive hydrothermal activity must be associated with the spreading process. Because of the relatively primitive capabilities available for seafloor exploration and the fact that exciting results were coming in from other areas of marine geophysics at the time, these suggestions were not followed up for over a decade. By then a host of indications had accumulated from seafloor and water-column studies that hydrothermal activity must be occurring. These were even persuasive enough to convince the National Science Foundation (NSF) to fund the study of an undiscovered phenomenon!

The authors have visited many black smokers in their studies, such as this one on the East Pacific Rise.

Dudley Foster/WHOI

Initial discoveries centered around the hydrothermal vents had ramifications throughout oceanography and beyond. The startling identification of a unique, highly evolved, and well developed chemosynthetic fauna associated with the vent fields proved that hot-spring activity had to be common. It also opened up an entirely new ecosystem to study. The chemical and physical properties of the high-temperature "black smoker" fluids showed them to be responsible for the transport and deposition of mineral ores. Concepts of massive sulfide-ore formation were revolutionized as fluid chemistry and fluxes were found to be important in supporting the chemical mass balance of the oceans themselves. The relatively uniform reactions between seawater and seafloor basalt constitute a geochemical "flywheel" that stabilizes the ocean's composition

against variations in river input caused by long-term climatic and tectonic changes. Physical Oceanographer Henry Stommel of the Woods Hole Oceanographic Institution had an idea (which seems to be holding up) that the input of thermal energy, the buoyancy flux, from the vents along the East Pacific Rise (EPR) drives the complex mid-depth circulation in the South Pacific.

Over the last 10 years, hydrothermal activity has been found in all oceanic volcano-tectonic regimes: at mid-ocean ridges over the entire range of spreading rates, on back-arc spreading centers, and on seamounts and submarine hot-spot volcanoes (see *Oceanus*, Winter 1991/92—Mid-Ocean Ridges— for definitions of terms and discussions of phenomena). The necessary ingredients are a large heat source emplaced in a permeable medium and a fluid. Because oceanic crust is formed by the injection of hot magma into a cold, tectonically active substrate, it is riddled with faults and thermal contraction cracks and is highly permeable. Since the hydrostatic pressure exerted by the oceanic water column is high (1,000 meters of water depth exerts 100 atmospheres of pressure), water saturates the crustal fissures and voids, and can be heated to very high temperatures without phase separation (boiling). Thus heat is removed very efficiently. There is a negligible loss of hydraulic head (hydrostatic pressure) as the fluid is emitted on the seafloor (unlike on land) and hence the fluid stream is stable with no "flashing" or geyser activity, much to the comfort of research submarine pilots. The ascending hot-water column generates an updraft around itself, further insulating the submarine from the effects of high temperature. Hot springs are therefore easily accessible for detailed sampling studies.


Stacy L. Kim/DSV *Alvin*

At 9°N on the East Pacific Rise, hydrothermal vent regions take on interesting shapes as minerals precipitate from the plume of hot water as it emerges from the vent.

Two Intractable Puzzles Emerge

When the first Galapagos vent analyses became available, two central problems were apparent that have proved intractable. The first concerns the magnitude of the global flux of hydrothermally altered seawater. The second is identification of the mechanism that controls the variable salinity of these fluids.

Global Flux of Hydrothermally Altered Seawater. Geochemical calculations of the oceanic mass balances of helium and strontium isotopes require that a volume of water equivalent to the entire ocean circulate through the ridge-crest hydrothermal system about every 10 million years, a very short time geologically. Vents are the overwhelming source of the rare helium isotope helium-3 in the oceanic water column. Extensive surveys of helium-3 distribution in the oceans have permitted quite accurate calculations of its inventory. Helium is a very insoluble gas; it is light enough to escape Earth's gravitational field via high-temperature regions in the upper atmosphere. Atmospheric concentrations are therefore extremely low. When deep water mixes into the surface layer, vent-derived helium escapes to the atmosphere, and eventually to space. The rate of this mixing has been calibrated using radioactive carbon to yield a "ventilation" or exposure-to-atmosphere time for the deep ocean

of about 1,000 years. From this information and the average helium concentration in the vent fluids, the fluxes of water, heat, and dissolved constituents can be determined.

Strontium has two major stable isotopes. Strontium-86 is nonradiogenic, whereas strontium-87 is produced by the decay of rubidium-87. Rubidium is relatively concentrated in continental crust by a variety of processes, so continental, fluvial (river-introduced) strontium has a higher strontium-87/strontium-86 ratio than does mantle-derived, hydrothermal strontium. Because strontium has a long residence time in the oceans, its isotope ratio in seawater is homogeneous. The strontium-87/strontium-86 ratio in seawater is 0.7091, intermediate between that in vent fluids (0.7035) and that in the average river (0.712). (The latter is an estimate based on measurements of most of the world's large rivers and many of their tributaries.) Combining these values with average strontium concentration data gives the hydrothermal flux required to balance the river inputs and maintain the observed seawater ratios. This flux calculation agrees with that based on the helium isotopes.

The glaring inconsistency suggests profound ignorance somewhere.

Now comes the puzzle: Early evidence for large-scale hydrothermal activity at spreading centers came from many geophysical observations in the 1960s and 1970s that conductive heat loss from oceanic crust generally increases with crustal age, to a steady-state value at several million to several tens of millions of years. This is the opposite of what would be expected if heat from the active vent areas were lost solely by conduction. The only alternative is large-scale convective cooling by circulating seawater. However, all calculations to date place an upper limit on the amount of heat transported in this manner that is equivalent to a fluid flux that is about one-fifth of that estimated from mass-balance calculations for helium and strontium isotopes. If arguments based on the thermal budget are correct, then deep-sea hydrothermal activity is an interesting, indeed beautiful, phenomenon—but not of great importance to the ocean's general geochemical cycle. If the flux based on isotopes is correct, however, then hydrothermal activity is of central importance. To date nobody has found any serious holes in either of the two approaches. The glaring inconsistency suggests profound ignorance somewhere. We (the geochemists), of course, are convinced that it lies in the geophysics....

Controlling Mechanism for Hydrothermal Fluid Salinity. Seawater entering the ridge crest hydrothermal system has a relatively constant salinity worldwide, but that of emerging vent fluids usually varies between fields, within a range of about one-third to more than double the original value. This is serious business, since high-temperature reactions consume all the seawater sulfate, precipitating it as metal sulfides, leaving chloride as the only significant anion (negatively charged molecule). Thus, from electroneutrality theory, the fluid's cation (positively charged molecule) transport properties are directly proportional to its chloride content. Chloride typically forms very soluble salts, and so is not likely to be precipitated in the water-rock reactions at high temperatures; this is a possibility, however, since there is scanty but tantalizing information on the natural occurrence of "green rust," an iron-hydroxy chloride in basalts whose chemistry shows they have been involved in hydrothermal reactions. While there is sufficient iron available in fresh basalts to affect chloride concentrations through formation

of this compound, it would need to have a peculiar chemistry: precipitating to produce low salinities under some conditions and redissolving to yield high salinities as the system properties change. This sounds like smoke and mirrors.

Vent animals explore the glassy broken pillow lavas on the East Pacific Rise.

The only alternative suggested to date is that deep in the system, seawater is heated to in excess of approximately 405°C. At this point phase separation occurs, producing a dense, high-salinity brine that coexists with a more voluminous, much fresher phase. This process has been observed both on a shallow seamount (where the phase-separation temperature was much lower) and on the EPR at 9°N where temperatures greater than 400°C were measured in fluids with salinities 100 times lower than that of seawater. The latter finding was in a ridge segment containing abundant evidence for very recent (within days) volcanism, with magmatic intrusions to shallow depths in the crust.

Two major puzzles exist with the phase-separation mechanism, however:

1) Measured temperatures at most hydrothermal vents on the EPR cluster within a narrow range around 350°C, more than 50° lower than the temperatures measured for phase separation, and these temperatures, where data exist, are often quite stable over many years; and

2) There are similar peculiarities in the salinity data.

Salinity values are typically far from the extremes produced by phase separation, and are also constant over time, often to within analytical error. Conductive cooling of vent fluids as they rise through the crust is negligible, given the short transit times (fractions of an hour) and the low thermal conductivity of basalts. It is difficult to imagine temperatures and salinities being controlled by subsurface mixing processes, since these are unlikely to be stable over periods of years. Time-series measurements provide very stringent constraints on a variety of geochemical and geophysical processes: If properties do not change over time, then chance cannot be in control; it must be something fundamental. In the case of ridge-crest hot springs, this realization has come slowly. The puzzles remain.

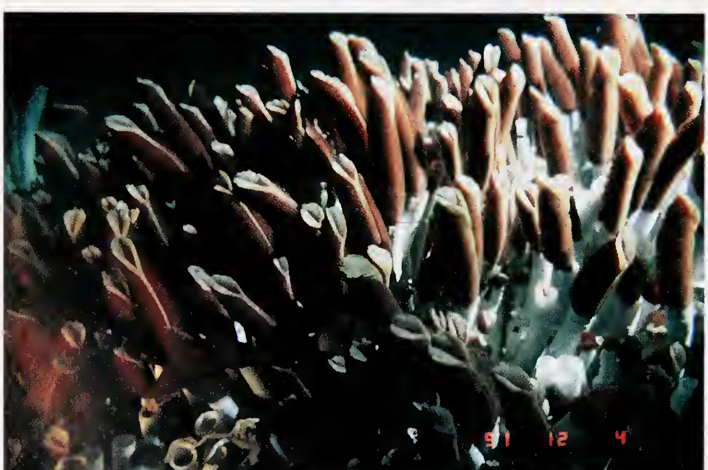
How We Are Attacking the Puzzles

The chemistry of a water sample is the result of many different processes that cannot be directly examined, and are not easily amenable to experimental manipulation. For example, we have not found a way to examine or collect the fluid rising beneath hot springs. In geophysics the interpretation of this kind of information is called an "inverse problem:" From results, one attempts to identify causes. The inversion is constrained by all relevant information. In geochemistry, the properties of the periodic table elements, including valence states (capacity to combine with other

elements) compounds formed, and isotopes (stable, radiogenic, and radioactive), can all be considered constraints. The various species are affected to markedly different degrees by particular processes, some strongly by one, others partially by several. Our strategy in attempting to understand the two major puzzles is to find indicator species that discriminate between hypothetical possibilities. For example isotopes of helium and strontium are powerful indicators of high, rather than low, global hydrothermal flux. Volatiles such as the rare gases are partitioned into the "less saline" component upon phase separation; however, the effect is small and may be obscured by sampling artifacts. A chloride-bearing phase, if it exists, must also precipitate bromide in the exact ratio found in seawater. Laws of structural chemistry make this highly unlikely. This exploitation of the resources of the periodic table is only about half complete, but methods for enlarging this fraction are under development.

Other Questions About Hydrothermal Activity Abound

While ridge-crest hydrothermal activity is now regarded as a normal oceanographic phenomenon, we actually know surprisingly little about it. In addition to the fundamental problems outlined above, there are deceptively simple questions outstanding: What is the relationship between spreading rate and hydrothermal output? Is it simply linear, or is it responsive to different tectonic styles and, hence, crustal permeabilities that accompany differing spreading rates? How long does a vent field last? Huge fields with millions of metric tons of precipitated sulfide ore have been discovered on the Mid-Atlantic Ridge and on Northeast Pacific ridges. However, on the faster-spreading systems of the Tropical and South Pacific, the many fields found to date are much smaller, on the order of tens of thousands of metric tons, or less. Are they soon buried by the more frequent eruptive events, or does a more fundamental reason explain this size difference? For example, one could ask: Where is the reaction zone located, relative to the chamber or plumbing system that supplies the fluid magma? What is the mechanism of heat exchange? How do a vent field's physical and chemical characteristics evolve over time? At 9°N on the EPR, we witnessed areally pervasive, chaotically disorganized venting, baked clams and tube worms that had not been scavenged, and an absence of usual biota around many of the vent fields. All evidence suggests an extremely young system. Elsewhere on the EPR, hot springs occur in small, discrete clusters separated from one another by several hundred meters to several kilometers of completely inactive terrain. Are these contrasting styles "snapshots" of different stages in the system's life cycle, or are they unrelated in time?



E. Garland/DSV *Alvin*

Hydrothermal vents support a varied and specialized fauna. Tube worms such as these from 9°N on the East Pacific Rise are an intriguing—if common—sight.

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There are equally fascinating biological questions. At 9°N the overwhelming presence of bacterial mats is unique among the systems observed so far. Among them, productivity is enormous. Sheets of hot water pour out of the bottom like inverted waterfalls, sweeping great clouds of bacteria into the water column. Approaching the ridge axis in DSV *Alvin* was like driving in a blizzard. Grazing organisms were rare. Do these mats provide an initial food source for immigrant larvae? (See Hydrothermal Vent Plumes: Larval Highways in the Deep Sea?, *Oceanus*, Fall 1991.) Why are these mats largely absent at the other EPR fields? The fauna found at the two Atlantic sites is distinctly different from that of the EPR: no big tube worms or clams; instead, there are swarms of shrimp, white anemones, and a peculiar solitary mussel that appears to be quite rare (see The Biology of Deep Sea Vents, *Oceanus*, Winter 1991/92). The vent fields found in the back-arc spreading systems of the Western Pacific appear to be more like the Atlantic in faunal characteristics than the Eastern Pacific. Are there grand faunal provinces separated by barriers of old, inactive crust? If so, these isolated provinces may be ancient, having diverged in their evolution after the last major episode of plate-tectonic reorganization both juxtaposed and fragmented preexisting provinces. One could go on.

The "discovery epoch" of the last 15 years was quite haphazard and uncoordinated, based on individual effort and luck. The RIDGE (Ridge Inter-Disciplinary Global Experiments) Initiative and InterRidge Program (see *Oceanus*, Winter 1991/92) have been developed to remedy this situation and replace it with a systematic approach involving much closer cooperation among oceanographic disciplines in the US and other countries. Many countries in Europe and the Pacific Rim are developing parallel programs. The hope, over the next decade, is to mount a global effort to advance our understanding of perhaps the most prominent, and certainly the most dynamic, feature on Earth, the spreading ridges in the deep ocean.

Rod Catanach/WHOI

Author John Edmond leaves DSV Alvin *following a dive to a hydrothermal vent field.*

John M. Edmond went directly to the Massachusetts Institute of Technology after finishing his formal studies in chemistry and geochemistry, and was bald in three years. He is interested in the processes controlling the chemistry of natural waters and associated sediments in space and time. He is a persistent, dedicated, and completely unsuccessful gardener, and also the doting father of two boys.

Karen L. Von Damm graduated from the MIT/WHOI Joint Program in Oceanography/Applied Ocean Science and Engineering after completing her thesis on the chemistry of black smokers. She spent several years at the United States Geological Survey at Menlo Park, California, and a spell with the Department of Energy. She recently accepted a position at the University of New Hampshire.

Focus on the Coast

The Black Sea: Threatened by Nature and Civilization

David G. Aubrey

The Black Sea is a microcosm of coastal areas worldwide. It is an "enclosed marginal sea," an oceanic basin separated from the open ocean by surrounding continents. It communicates with the Mediterranean Sea through the narrow Bosporus Strait into another marginal sea, Marmara, then through the Dardanelles to the Aegean Sea. The Black Sea serves as the drainage basin for major European rivers as well as those of northern Asia. Rivers flowing into the western Black Sea carry more than 90 percent of the fresh waters entering the basin, much of it polluted from industrial and agricultural discharge from eastern Europe and Asia. The Danube, for example, is acknowledged to be one of Europe's most polluted rivers, though its effects on Black Sea water quality are poorly documented.

As the largest oxygen-depleted body of water in the world, the Black Sea is analogous to primordial seas, where much of today's petroleum resources were generated. Although the Sea exceeds 2,000 meters in depth, only the upper layer of 100 meters or less contains any oxygen. Below this oxygenated surface layer the water is rich in hydrogen sulfide, a reduced form of sulfur that occurs where oxygen is absent. Hydrogen sulfide is characterized by its rotten-egg smell. In fact, as scientific instruments are raised through the Sea's oxygen-poor water up to the surface, their metal surfaces are stained black and the rotten, sulfurous smell permeates the deck. Even water samples themselves smell of rotten eggs.

From the early days of civilization, the Black Sea has been misunderstood and mistreated. When the Greeks first encountered this region, they called it *Pontos Euxenos*, meaning Hospitable or Friendly Sea, as the waters at first appear to be benign and easily navigable. But as the Greeks and Romans came to experience this sea's violent storms, it became known instead as the Black Sea. The Turkish apply this same name, as a contrast to the more hospitable White Sea (or Mediterranean Sea) that borders their southern coast. Strangely enough, we now use the term "euxinic" to describe a stagnant sea with toxic bottom waters (including the Black Sea), a far cry from the word's original meaning of "hospitable."

Today we know the Black Sea is anything but hospitable. Many natural conditions have combined to produce a marine environment that is unique among modern oceans, including:

- restricted circulation (due to its unusual basin topography),
- steady freshwater inflow (from major rivers of the northwest Black Sea),
- continuous saltwater flow through the Bosporus Strait, and
- thousands of years of salty conditions.

Stratification—and Decreased Biodiversity

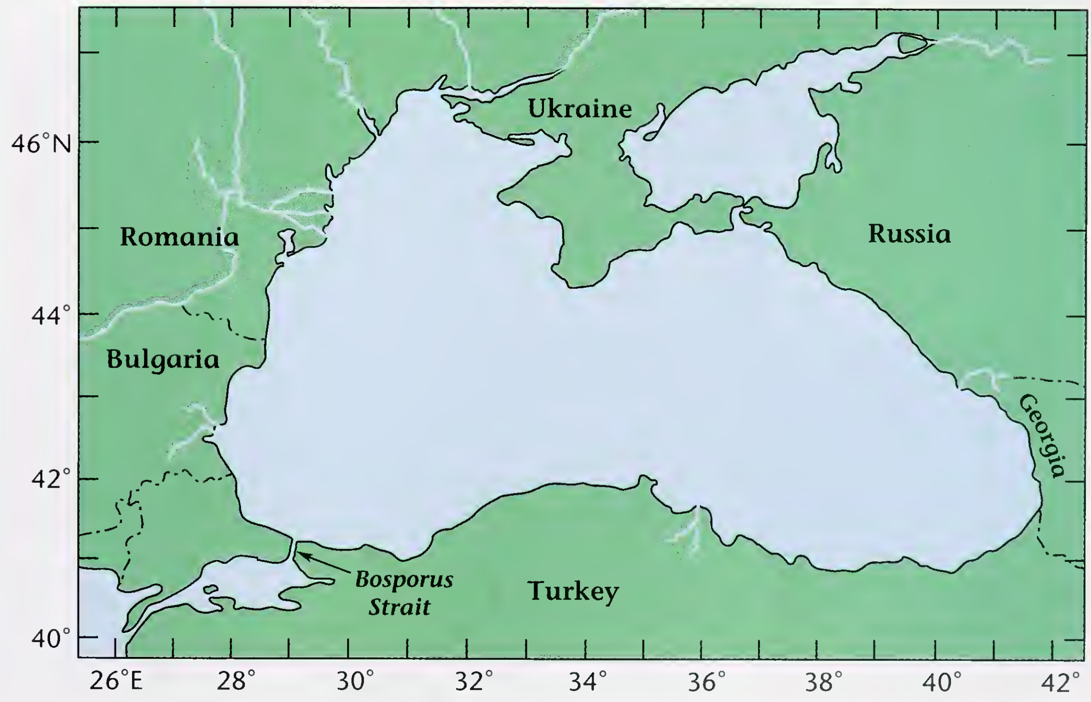
The natural result of these physical, chemical, and geological coincidences is a strongly stratified ecosystem. Below 100 meters, it is largely devoid of life, and biological activity is limited to anaerobic bacteria. In the surface waters above 100 meters, a more balanced ecosystem used to thrive. Due to the strong river

inflow, however, the surface waters are relatively fresh, with a salinity of about 15 to 18 practical salinity units (psu), which is low compared to open-ocean values of about 34 psu, or the deep Black Sea salinity of about 24 psu. This low surface-salinity places the upper Black Sea waters in the "estuarine" class of salinities, which is a very different habitat than the higher salinity waters of some coastal oceans.

Human activities have exacerbated this natural limitation. The land around the Black Sea has been inhabited for nearly 10,000 years. Overfishing, coastal development, and, more recently, massive air and river pollution have all accelerated the decline in the Black Sea's environmental quality. Fisheries have collapsed from a combination of overfishing and high nutrient loading from river input. Excessive nutrient input has also created "sour water," which is caused by frequent and intense phytoplankton blooms that strip the water of oxygen. Such adverse water quality has created bottom pockets of hydrogen sulfide in waters as shallow as 15 meters, killing all life that contacts them, and has reduced the attraction of tourists to the Romanian and Bulgarian coasts.

How did this condition of increased chemical pollution and eutrophication come about? What can we do about it? These questions are being addressed now for the first time, as the political transition within the Eastern bloc has enhanced communication among the Black Sea coastal countries (Bulgaria, Georgia, Romania, Russia, Turkey, and Ukraine). Whereas former governments in the Eastern bloc had only limited environmental controls, present governments are working to implement stricter environmental regulations and encourage cleanup. To be effective, the governments must understand the primary causes of the Black Sea's degradation, and work efficiently toward improvement. Fundamental questions that can be addressed by marine scientists abound:

- Where does the worst pollution come from? Is it from river input, atmospheric fallout, or a variety of nonpoint sources distributed around the Black Sea coast?
- Of the various sources, which are the worst offenders? What ecological problems are caused by each source, and how can the effects be measured and eventually remedied?
- For cleanup, is source-control the best solution? Or do innovative technologies exist that may contribute to



Jack Cook/WHOI Graphics

the cleanup of pollution "hot spots" within the Black Sea itself?

Such questions must be resolved if cleanup efforts are to be successful, as the limited financial and human resources available must be efficiently focused on the most appropriate areas to be effective. To help accomplish these goals, several efforts are under way to coordinate the activities of the coastal Black Sea countries.

Coordinating Cleanup Activities

The United Nations Environment Program (UNEP) is creating a Black Sea Action Plan to help promote a coordinated, uniform response to Black Sea pollution. In addition, a Convention for the Protection of the Black Sea Against Pollution has been drafted for signature by the environmental ministries of the coastal Black Sea countries. Its signature, scheduled for June 1991 in Constantsa, Romania, was delayed by the collapse of the former USSR. Establishment of the Commonwealth of Independent States (CIS) and declarations of independence of Georgia, Russia, and Ukraine increase the need for coordination among the newly independent republics. The environmental ministries of all governments have affirmed both the need for a convention and their intention to implement one as soon as feasible. Since the Convention carries financial obligations with it, the signing may be postponed until the economies of these countries solidify.

To address fundamental scientific and monitoring goals, all the coastal Black Sea countries (except Georgia, for the time being) have developed a Cooperative Marine Science Program for the Black Sea. The Woods Hole Oceanographic Institution played a lead role in forming this Program, and has members on its steering committee. In September 1991 the Program conducted a successful, five-ship Black Sea cruise, obtaining (for the first time) information on the physics, biology, and chemistry of its entire volume. The entire Black Sea's circulation now can be inferred from direct, synoptic (nearly simultaneous) measurements, instead of extrapolating from climatological data or relying on data obtained from different time periods and cruises. The Program also sponsored an international workshop in Varna, Bulgaria, in October 1991, to investigate the Black Sea's health. This successful workshop brought experts together to share data on the Black Sea's condition and to provide a forum for coordinating scientific research and environmental monitoring toward more effective environmental quality protection.

What does the future hold? Recent rapid changes in eastern Europe have opened the door for new scientific opportunities and environmental improvement in this region. Because many countries of both western and eastern Europe contribute to Black Sea pollution, environmental improvement requires cooperation at all levels and coordination of pollution controls for all these countries. International coordination and participation is essential if this once healthy, now threatened, sea is to recover.

David G. Aubrey is a Senior Scientist in the Department of Geology and Geophysics and immediate past Director of the Coastal Research Center at the Woods Hole Oceanographic Institution.

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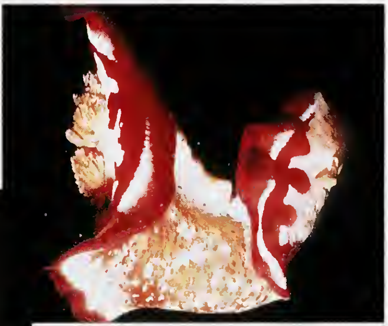
Creature Feature

The Spanish Dancer Nudibranch

Joseph R. Pawlik

Disturbed from its resting place on a Pacific coral reef, the Spanish dancer nudibranch (*Hexabranchus sanguineus*) displays the red and white margins of its mantle as if to say, *Back Off!* These brightly colored marine slugs lack the hard shell that encloses most other molluscs, including snails, clams, and oysters. Instead, these and other nudibranchs in the suborder Doridacea protect themselves with distasteful chemical compounds. The Spanish dancer's defensive compounds, trisoxazole macrolides, are derived from a black sponge, *Halichondria* sp., that the nudibranch eats. Stored in the nudibranch's body wall, the macrolides repel attacks by voracious reef fish and crabs. High concentrations of macrolides are also found in this slug's beautiful egg ribbon where in addition to foiling predators they may also prevent the growth of pathogenic microorganisms.

The Spanish dancer is one of the largest (to 25 centimeters) and most active nudibranch molluscs, and is a common and conspicuous inhabitant of coral reefs throughout the Indo-Pacific. Unlike most nudibranchs, *H. sanguineus* has a spectacular swimming pattern: Its body is thrown into sweeping head-to-toe flexions that undulate through its vivid mantle margins. Herein lies the origin of the nudibranch's common name, as the patterns seem to simulate a flamenco dancer's gyrations. This animal was photographed from above, with its head pointed down. The two projections on its head, called



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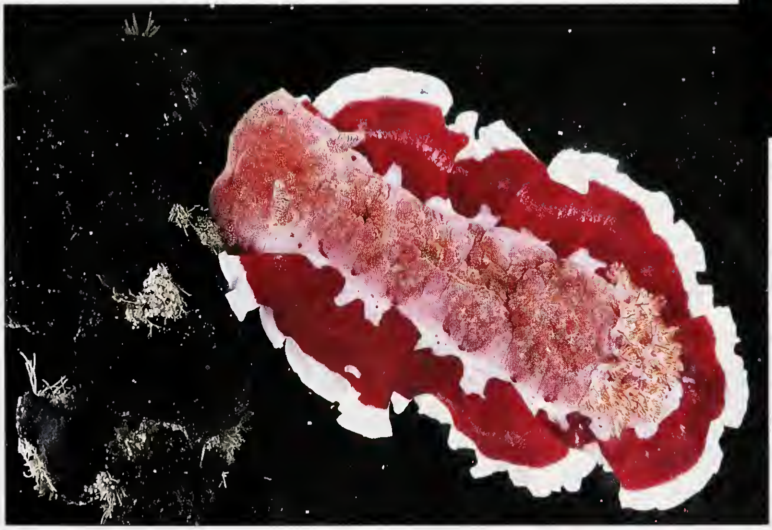

Joseph R. Pawlik

The Spanish dancer nudibranch is vibrantly colored, and well protected with its chemical defense system. This marine slug earned its name by swimming in a pattern reminiscent of a flamenco dancer, as at upper right. (Upper right photo from Seven Underwater Wonders of the World, *to be published in October 1992.)*

rhinophores (literally "nose-bearers"), sense and locate both prey sponges and prospective mates. The nudibranch's gill is the frilly, branched structure at the top of the photo. The dark red and white mantle margin is very thin, so all the body organs are contained within the pink region.

All dorid nudibranchs are simultaneous hermaphrodites, meaning that they function as males and females at the same time. This reproductive adaptation may have evolved to insure the fertilization of as many eggs as possible during their infrequent and very brief mating encounters. After mating, Spanish dancers lay their eggs in coiled ribbons on coral rubble. The eggs hatch after several days, releasing

Burt Jones & Maurine Shimlock

Although lovely to look at, the Spanish dancer nudibranch's egg case is bad tasting at best—and toxic at worst.

microscopic planktonic larvae that require several weeks of development before metamorphosing into tiny juvenile slugs. The stimulus for this transformation has not yet been identified, but metamorphosis probably occurs when the larvae settle on one of the few sponge species that the adults eat.

The noxious metabolites harbored in sponge tissues make this "food" unavailable to most invertebrates and fishes, but sponge prey is a specialty of dorid nudibranchs. The bright, warning-color patterns of marine slugs like the Spanish dancer probably evolved in concert with the loss of their protective shells and the emerging use of chemical defense derived from their diets. For these slugs, then, the best defense is something offensive!

Joseph R. Pawlik is Assistant Professor of Biological Sciences and Center for Marine Research at the University of North Carolina, Wilmington.

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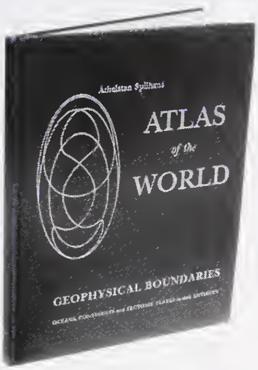
Books Reviewed



Atlas of the World

By Athelstan Spilhaus, 1991. American Philosophical Society, Philadelphia, PA. 92 pp. – $45.

Geography is a hot topic, and the National Geographic Society is helping to raise the temperature. The Society has launched a campaign to return the study of geography to the American classroom. Public television has done likewise, using the children's educational TV show, "Where in the World is Carmen Sandiego?" This campaign can only serve to create renewed interest in maps for students and educators alike, and hopefully these geographically attuned troops can be exposed to the world as projected by Athelstan Spilhaus in his new *Atlas of the World*.

All too often the world is represented in a Mercator projection, that familiar rectangle of the world centered on the Western Hemisphere with neat, rectangular grids of latitude and longitude. Spilhaus reminds us that Gerardus Mercator's 16th century map was a navigational tool for seamen. It grossly distorts land masses and ocean areas near the poles—polar areas were untraveled and unknown in Mercator's time. Now we need a successor to Mercator's map in a more equal-area projection for those scholars, students, and explorers of the ocean interested in more than transiting its surface. Spilhaus's *Atlas of the World* is such a successor.

In his book, Spilhaus offers us a variety of projections and views of the world (ocean and land) along with a literate history of his whole-ocean maps, the evolution and explanation of various map projections, and a guide to the vocabulary that mapmakers use to describe their products. The atlas's 29 full-page, color maps are accompanied by helpful annotations, 39 black-and-white maps that enhance and explain the color works, and 12 additional instructive figures. Some of the maps are hand-drawn, some computer generated. The quality of the color maps is uneven, but this never interferes with their content. The maps are divided into three sections: shoreline maps, composite shoreline maps, and tectonic plate margins.

The first section covers maps with continental shorelines as natural boundaries, offering 11 different views of the world using varied projections, some equal-area, some conformal, yet all deriving their perimeter from continental shorelines, keeping the world ocean intact. In Shoreline Map X, Spilhaus annotates that this oblique, normal August conformal projection (he provides a good glossary to help novices with the terminology) may be disturbing since it displaces North America from South America, but "it simply emphasizes that the bulk of North America is not north of South America." This statement is heresy to anyone who has only observed the world on a Mercator projection. Yet this new illustration stimulates the eye and the mind for further world viewing, and opens the door for the variety of world perspectives that Spilhaus offers us.

The second category of composite shoreline maps with continental shorelines as natural boundaries offers 10 color maps that minimize even further the distortion of the shapes of continents and oceans by dividing the world into segments that are then assembled into a whole. This section of interrupted world maps, Spilhaus says, may "detract from the unity of the whole earth

which we attempt to portray. The interruptions in this atlas at least have the merit of being along natural boundaries."

The final section of the atlas focuses on the tectonic plate margins as natural boundaries, and offers equal-area maps and illustrations of continental drift. Geophysicists and geologists in the late 20th century are mapping plate margins at very high resolutions and examining these margins in detail. The maps in this section of the atlas are instructive on a global scale. The atlas's final map, Tectonic Plate Margin Map XXIX, shows the position of land masses for three eras from Early Cambrian, Late Carboniferous, to the Present on a centered transverse Hammer equal-area projection (looking like a figure-8 with almost no waist), and is annotated by Spilhaus as "a storyboard for the movement of landmasses through time."

His use of the term "storyboard" creeps in from another of his careers as creator in the 1960s of the science-oriented comic strip, "Our New Age." Spilhaus was profiled in *Oceanus* (Winter 1987) five years ago as an inventor, scientist, engineer, author, raconteur, comic-strip creator, professor, dean, institute president, sculptor, architect-designer, toy collector, meteorologist, advisor to US presidents, and father of the Sea Grant College concept. That list neglected to mention his cartographic leanings. Spilhaus's career as a mapmaker goes back to the 1940s, and continues with his latest production, *Atlas of the World*. Having seen him at work with pens and small bottles of colored ink, pieces of the world cut and scattered about as he assembled some of the composite maps, I balance my knowledge of him as scientist with my image of him as the mapmaker, the artist.

If it is through maps that we think we know the world, then the material in Spilhaus's *Atlas of the World* is encased in a technical setting beyond the reach of most curious young geographers. It will serve well in its current form for those scholars, students, and explorers of the ocean interested in more than transiting its surface. I hope it can also be translated into another less-technical and more widely distributed setting so that Spilhaus's perspectives and projections can stimulate our quest for the image of our real world.

—Judith Fenwick
Research Associate
Department of Geology & Geophysics
Woods Hole Oceanographic Institution

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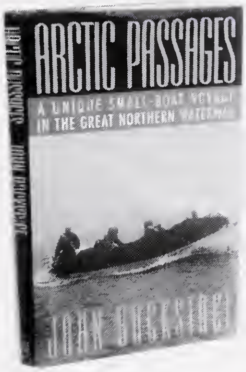


Arctic Passages

By John Bockstoce, 1991. William Morrow & Company, Inc., New York, NY; 256 pp. – $22.95.

It is mid-July and throughout most of the US people are struggling with heat near or above the centennial mark and slogging through air viscous with clinging humidity. Just the time, methinks, to crack open John Bockstoce's *Arctic Passages, A Unique Small-Boat Voyage in the Great Northern Waterway*, and retreat to the cold comfort of the northern quarter of our continent. Besides, I've a friend who, at the time of my reading, is pointing his yacht up and into those high, icy waters. And equally as apt, it was almost a year to date that I was setting sail on the yacht *Warbaby* into the Labrador Sea, making for Greenland.

Truth be told, this arm-chair air-conditioning, though a small mid-summer blessing, doesn't quite match the penetrating chill of hours, days, weeks, months outside in damp oilskins exposed to freezing drizzles, ice-spiked winds, and the pervasive spray and splash of frigid, berg-bound waters. For a change, it was better to shiver between the covers of a book.

Nevertheless, whatever your bent—be it an interest in the Arctic, its exploration, and navigation; the history, culture and present-day life of Alaskan and Canadian Eskimo peoples; the history of native and Euro-American whaling; or, plain ol'adventure—*Arctic Passages* is well worth the read. Indeed, for those of this ilk, the book will be a double pleasure; a cold climate exploration "two-fer." Bockstoce chronicles two decades of small-boat voyaging in the Northwest Passage. As Tim Severin once westered the North Atlantic to Thule and beyond—tagging in St. Brendan's purported wake—Bockstoce, in the book's first part, wends eastward, also with a skin-clad hull holding him afloat. The second recounts his completion of the entire Passage in *Belvedere*, a steel-hulled, motor/sail, long-range cruiser.

As a student of, and initiated participant in, coastal Alaskan Eskimo life, Bockstoce learned early on of the wondrous seaworthiness of traditionally designed native boats. In particular, the umiak—the Eskimo's formidable lashed-wood-frame, walrus-hide-flanked, cargo and hunting vessel. Bockstoce details his quest for a mentor, and his subsequent attainment of highly specialized umiak building and seafaring skills—much of the latter learned by trial and error. The umiak voyaged in tandem with a Boston Whaler in the early years, and a motor-propelled cargo canoe in the later ones.

The expedition's advance, given the vagaries of Arctic weather and the vicissitudes of Arctic ice—and the brevity of the polar summer—was achieved piecemeal, usually in a "one step forward, two steps back" fashion. Dogged, intrepid, and visionary, Bockstoce picks his way eastward year after year, starting out anew where he left off a year, or a couple of years, back—he even has to return to "Go" (far western Alaska), after having made significant progress eastward. The umiak's walrus skins only remain safe and serviceable for three years. Rehulling (and winter storm damage repair) has been a necessity. Ultimately, though far into the remote and treacherous passages (e.g., uncharted rocks and shoals, nine-knot tidal races, shifting pack ice, dissolving and abandoned artificial oil-drilling islands) of the Canadian Archipelago, the three-year "warantee" expires and, with the distance now too great to return for a proper "refit," Bockstoce and crew know they must call it a day.

The story ain't over. As the director of a whaling museum and a pre-eminent scholar in the field, Bockstoce has a consuming and legitimate need to explore the old domains of the western and eastern whaling fleets. It is thus that he comes to purchase *Belvedere* and, thereby, gains the wherewithall to eventually—after another, albeit lesser, sequence of fits and starts—lay valid claim to having been the first yachtsman to bring a boat through the Northwest passage, west to east—Alaska to Greenland to New England to New York City. The first page of *The New York Times*, the Tilman Medal, and a place in history follow.

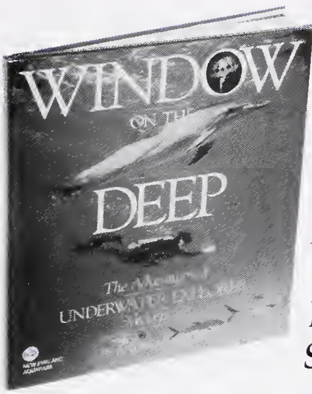
The length and peripatetic, intermittent nature of these voyages has given Bockstoce the opportunity to tell his readers of encounters with the people who live in the ports, villages, and hunting and fishing camps he puts in at—and of others met who visit, tarry, and work in these cold regions. The two-decade span allows him to describe the changes the Arctic has undergone during a period of accelerated change—namely the effects wrought by the oil boom, and, in Canada's case, bust. He has several changes of crew, including his new wife and their son, with whom the reader becomes acquainted.

Bockstoce talks in a direct voice, his manner being clear and straightforward. While his exploits are courageous ones, and, of course, somewhat adventurous—the best explorers try to minimize harrowing undertakings. He has, all the while, been concomitantly engaged in serious professional research, hence his tales are satisfyingly bereft of hyperventilated macho, mock heroics. He takes us to wonderful places—and some not so; he describes the awesome qualities of high latitude atmospherics, weathers, and terrain; wildlife is far from neglected, as whales to billions too many mosquitoes find niches in these pages. While he shies from waxing rhapsodic, he is comprehensive about including, with equanimity, his responses to and observations of all the phenomena—natural, historical, cultural, and personal—encountered along the way. There is throughout an undercurrent that the environment of the North is fragile, requiring persistent vigilance and action to preserve its still mostly pristine nature.

All in all, *Arctic Passages* comes off as if you might be a friend of the author's, or one of his circle, and are sitting around with him listening to his firsthand tales about what he has been spending so much of his life doing. Indeed, I closed the book wishing I did know him personally, and that I had had the opportunity to sail with him (more so in the yacht than the umiak, to be honest). Despite the all-too-familiar discomforts of Arctic/Antarctic seaborne travel, he inspired me to seek another opportunity for it. In the book he hints at what he has discovered and learned about this immense region and its histories. This knowledge has become the fabric of a slew of other books from his hand—I know I, and other readers not already familiar with those books, will turn to them soon after reading this, his most recent book.

There is, alas one regret worth noting; *Arctic Passages* is very amply illustrated with photographs by the author and others who have traveled with him—including two on assignment for the National Geographic Society. Unfortunately, the photographs are reproduced in black and white and printed on the same paper stock as the print—sadly, a formula for muddied tones and dimunition of detail and effect; 'twould that it were otherwise.

—Stuart D. Klipper
Artist/Photographer



Window on the Deep: The Adventures of Underwater Explorer Sylvia Earle

By Andrea Conley, 1991. A New England Aquarium Book, Franklin Watts, NY; 41 pp. – $13.95.

Sylvia A. Earle, who recently announced her resignation as chief scientist of the National Oceanic and Atmospheric Administration (NOAA), has lived a life of daring and adventure. One of the world's foremost divers, she has ventured, untethered, to the record-breaking depth of 1,250 feet. Earle was also one of the first three pilots to take a one-person submersible to a depth of 3,000 feet. Several species of marine life bear her name. At 56, she has lived a thrilling, exemplary life, and is a fit role model for young people, both boys and girls, who might someday follow in her footsteps.

For that reason, I greeted with pleasure the interesting-looking book about her that has been written by Andrea Conley of the New England Aquarium in Boston. At first glance, my eager anticipation was rewarded. There are more than 20 pages of gorgeous full-color photographs of Earle at work. I sat down to read the book, hoping that the text would answer many questions I had about Earle as an individual and as a scientist. What motivated her? What did it feel like to dive alone in a submersible to 3,000 feet?

I anticipated a book whose tone would be immediate and give me a first-hand look at this fascinating person. But I was disappointed. Unbelievably, there are almost no direct quotes from Sylvia at all, and precious little insight into her mind-set. Use of the passive voice abounds, as in the book's only reference to Sylvia's childhood (remember, this is a children's book): "She had made a habit of recording her adventures on paper ever since she'd first observed wildlife in the pond behind her childhood home in New Jersey." Where is Sylvia in this book about Sylvia?

Wondering if my judgment was off, I showed the book to some children. Alex (age 6) was awe-struck by the photographs. Rachel (age 10) and Eliza (age 12) read earnestly for some time, but finally put the book down, begging me to let them stop. "It's boring," they explained.

Though I shared their reaction, I wondered if the problem was that Rachel and Eliza weren't particularly scientifically inclined. So I showed the book to Lizzie, as voracious and wondering a nine-year-old scientist as I've ever met. (She might even be a Sylvia Earle in the making.) Lizzie's eyes widened when she saw what the book was about. At first, she devoured the material, exclaiming with joy at the photographs. "Read a little of the text," I urged her. She read for a while, then said, disappointed, "Why don't they tell us what she saw?" (In literal fact, there are many descriptions of what Sylvia saw, but they are presented in such a distant manner that any sense of the thrill of observation and discovery is obliterated.)

I had a couple of other questions about the book. There are two pages at the end that summarize the highlights of diving history. But, curiously, the submersible *Alvin* is not mentioned. Also, the book came out several months after Dr. Earle was appointed Chief Scientist at NOAA, but this significant achievement was not noted. Perhaps the book was already completed by that time.

Writing books for children about role models such as Sylvia Earle is very important

work. Children are hungry for information about the ocean, and about ocean scientists. They yearn for chances to understand the mind-sets of those who choose this career. This book appeared to offer that type of insight. I was disappointed that its promise was not borne out.

—Deborah Kovacs
Author of children's literature, and
Editor, *Ocean Explorer,*
the newsletter for Young Associates of the Woods Hole Oceanographic Institution

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Transforming Traditions in American Biology, 1880-1915 by Jane Maienschein; 1991; The Johns Hopkins University Press, Baltimore, MD; 366 pp. - $48.

The Ecology of Fishes on Coral Reefs edited by Peter F. Sale; 1991; Academic Press, San Diego, CA; 754 pp. - $69.95.

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Boojums All The Way Through: Communicating Science In A Prosaic Age by N. David Mermin; 1990; Cambridge University Press, New York, NY; 223 pp. - $16.95.

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At The Sea's Edge: An Introduction to Coastal Oceanography for the Amateur Naturalist by William T. Fox; 1991; Prentice-Hall, Inc., New York, NY; 316 pp. - $13.95.

Colors Of The Deep by Jeffrey L. Rotman and Joseph S. Levine; 1991; Thomasson-Grant, Charlottesville, VA; 144 pp. - $45.

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Dynamics of Marine Ecosystems: Biological-Physical Interactions in the Ocean by K.H. Mann and J.R.N. Lazier; 1991; Blackwell Scientific Publications, Inc., Cambridge, MA; 432 pp. - $44.95.

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VIDEOS

The Earth Explored: Plate Tectonics—A Revolution in the Earth Sciences produced by Penn State Audio-Visual Services, University Park, PA; 30 min.; rental $19.

Aquaculture produced by Films For the Humanities & Sciences, Princeton, NJ; 26 min.; purchase $149; rental $75.

Reflections on Waves: Electromagnetism, Parabolic Antennas, the Doppler Effect, and Electromagnetic Radiation produced by BBC for the British Open University; Penn State Audio-Visual Services, University Park, PA; 30 min.; rental $19.

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Oceans (ages 10 and up) by Philip Whitfield; 1991; Viking Children's Books, New York, NY; 71 pp. - $15.95.

Night Reef: Dusk to Dawn on a Coral Reef (ages 10 to 14) by William Sargent; 1991; New England Aquarium, Boston, MA; 41 pp. - $13.95.

Sailing to the Sea (ages 6 to 12) by Mary Claire Helldorfer and Loretta Krupinski; 1991; Viking Penguin, New York, NY.

A Child's Treasury of Seaside Verse (ages 7 and up) compiled by Mark Daniel; 1991; Dial Books for Young Readers, New York, NY; 137 pp. - $16.95.

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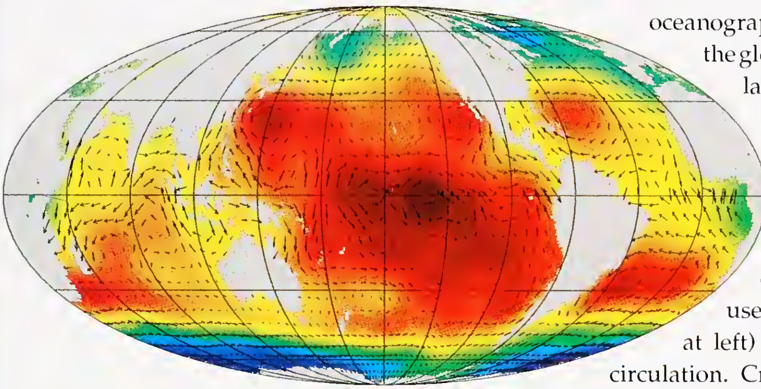

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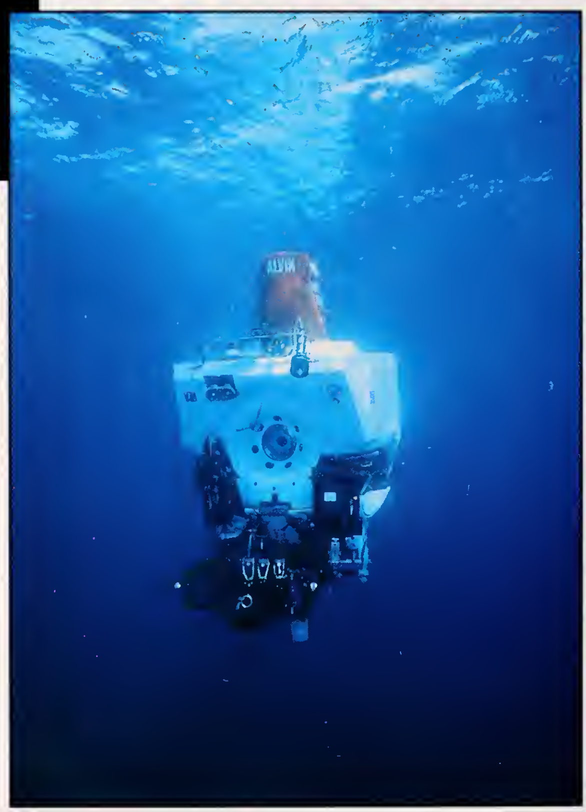

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